X-Ray Crystallography

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1 Preliminary Information

In this report, the structure of $Ca_5F_{0.96}Cl_{0.04}(PO_4)_3$ (Apatite) with formula units per unit cell of $Z = 2$ was investigated. In exercise 2, we determined that due to absorption effects the maximum spherical size for a single crystal that may be used for x-ray diffraction using Cu-K_α is 108μm. The density of the crystal is 504.9 $\frac{g}{mol}$

2 XRD Background Theory

The goal of x-ray diffraction crystallography (XRD) is to determine the structure of a given material by means of subjecting it to x-ray radiation. Any given atom in a crystal lattice will elastically scatter (diffract) the incoming photons according to Bragg's law (eq. 1), so long as the wavelength is not such that the electrons absorb and re-emit the incoming photon. This would be inelastic scattering and is the reason high energy x-rays are used in XRD.

$$n\lambda = 2d_{hkl}\sin\theta \tag{1}$$

The measured intensities of the scattered photons are proportional to the absolute value of the structure factor, F_{hkl}, squared, as well as several correction terms, including the polarization factor, a geometric factor, and an absorption coefficient. The structure factor is the Fourier transform of the electronic density, and can be calculated as follows:

$$F_{hkl} = \sum_{j=1}^{N} f_j \exp[2\pi i(hx_j + ky_j + lz_j)]. \tag{2}$$

Here, f_j is the scattering factor for atom j, which largely depends on the number of electrons contained by the atom. One can calculate the Intensities from the structure factor, but not vise versa, as the phase information is lost. Only the magnitude of F_{hkl} can be calculated from the intensities. Unfortunately, the detector only measures intensities. To find the atomic positions, we must first recover the structure factors using a pre-existing model, essentially a preliminary guess to check self-consistency. The structure factor then allows us to calculate the electronic densities, $\rho(x, y, z)$ via equation (3), which in turn, leads to the atomic positions.

$$\rho(x, y, z) = \frac{1}{V}\sum_{h,k,l} F_{hkl} \exp\left[-2\pi i\left(h\frac{x}{a} + k\frac{y}{b} + l\frac{z}{c}\right)\right] \tag{3}$$

2.1 Patterson Method

Patterson synthesis is useful in structural determination, because it only requires knowing the magnitude of the structure factor, $|F_{hkl}|$, which we can calculate from the measured intensities and the aforementioned correction factors. The Patterson function is defined as:

$$P(u, v, w) = \sum_{h,k,l} |F_{hkl}|^2 e^{-2\pi i(hu+kv+lw)}. \tag{4}$$

$P(u, v, w)$ will have the largest peaks wherever $p(x, y, z)$ is also the largest, thus the Patterson peaks correspond to electronic densities, and the highest peaks will correspond to the largest atoms (largest in the sense of greatest having more electrons and thus a higher atomic number). Thus, the distances between the Patterson peaks correspond to interatomic spacing; for materials with a few heavier atoms present, this method is especially useful. Comparing interatomic distances to those of the starting model allows for the determination of atomic positions.

2.2 Direct Determination Method

To recover the lost phase information in the structure factor, we can calculate the normalized structure factor, E_{hkl}, and determine if the structure is centrosymmetric via equation 6.

$$E_{hkl}^2 = \frac{F_{hkl}^2}{\langle F_{hkl}^2 \rangle} \tag{5}$$

$$\langle\ |E_{hkl}^2 - 1|\ \rangle = \begin{cases} 0.968 \text{ centrosymmetric} \\ 0.736 \text{ non-centrosymmetric} \end{cases} \tag{6}$$

In 1952, American physicist David Sayre introduced an equation that allows for the calcualtion of structure factor phases for some reflections based on known structure factors.

$$F_{hkl} = \sum_{h'k'l'} F_{h'k'l'} \cdot F_{h-h',k-k',l-l'} \tag{7}$$

For centrosymmetric structures the phases can only be 0 or π, so the Sayre equation can be reduced even further. The goal of structure refinement is the minimize difference between the calculated structure factor and the model, i.e. $\Delta_1 = |F_0| - |F_c|$ and $\Delta_2 = |F_0^2 - F_c^2|$, using the least squares method.

3 Sample Preparation and Data Collection

First we cleaned a glass coverslip and placed a drop of DI water on it. Then we add a few crystals into the water, and scraped a few single crystals away in order to choose a one closest to the maximum allowed size for the diffraction. To mount the crystal for experimentation, we placed some putty in a heavy cylinder and inserted a thin needle through. Next, we added some glue on the tip of the needle and attached the chosen grain. We then placed the mounted sample into the x-ray diffractometer and adjusted the screws while rotating between the 0,90,180, and 270 degree positions to ensure the crystal was centered throughout its entire rotation on the view finder.

Data was collected over a period of 21 hours with a $\Delta\phi$ of $0.5°$.

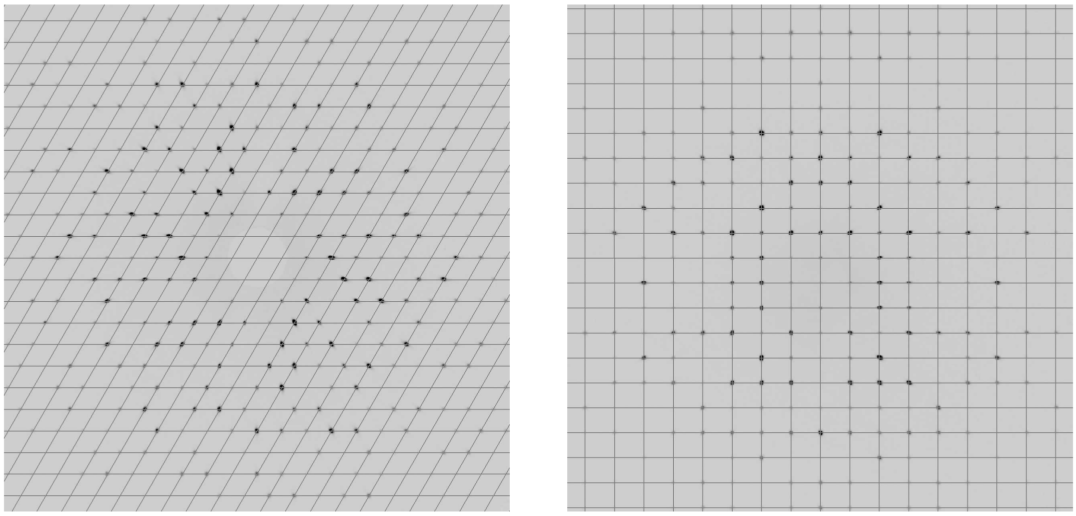
3.1 Least Squares Method

To calcuate the error for each iteration of model improvement, the least squares method is used. The loss function (residual) is calculated as the sum of the squared differences of model positions and the measured positions (Eq. **??**).

$$r_i = \tag{8}$$

4 Resulting Structure

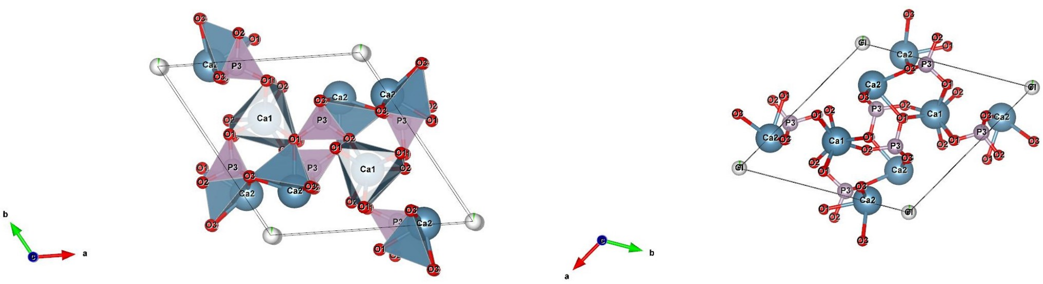
The calculated $(E^2_{\mathrm{hkl}} - 1)$ value was 0.974 and the determined space group was $176(6_3/\mathrm{m})$.



(a) hk0 plane

(b) 2kl plane

Figure 1: Here are two different hkl planes



(a) along c direction

(b) along a direction

Figure 2: Here are two views of the same structure generated by VESTA. In case the labels are too small to read, white is O, red is H, blue is Ca and purple is P.

Table 1: Here are the cell parameters calculated by *CrysAlisPro*.

Cell parameters	**value**
a	9.3968(6) Å
b	9.3968(6) Å
c	6.8854(0) Å
α	90.000(0)°
β	90.000(0)°
γ	120.000(0)°
Volume	526.53266(6) Å^3

Table 2: Below are the calculated BVS values of the cations calculated via modification of the excel sheet made in the final exercise of this course.

Direct method		**Patterson method**	
cation	BVS	cation	BVS
Ca_1	1.8651	Ca_1	1.8652
Ca_2	2.0277	Ca_2	2.0335
P	4.9791	P	4.9788

Table 3: Here are the atomic positions calculated by both the direct method and the Patterson method.

		Direct method			**Patterson method**		
Atom	Wyckoff position	x	y	z	x	y	z
Ca_1	6h	0.249206	0.242123	0.250000	0.750796	0.757878	0.250000
Ca_2	4f	0.666667	0.333333	0.001163	0.333333	0.666667	0.498836
P	6h	0.601526	0.0.630994	0.250000	0.970535	0.601526	0.250000
F	2a	0.000000	0.000000	0.250000	1.000000	1.000000	0.250000
O_1	6h	0.412079	0.533297	0.250000	1.157439	0.672834	0.250000
O_2	6h	0.672833	0.515391	0.250000	0.878784	0.412081	0.250000
O_3	12i	0.658210	0.742762	0.070452	0.915447	0.658210	0.070446
Cl	2a	0.000000	0.000000	0.126183	1.000000	1.000000	0.125501

5 Discussion

crystal chemistry, bonding angle, bond distance, topology

6 Bibliography

Ripoll, Martin Martinez. The Patterson Function and the Patterson Method, www.xtal.iqfr.csic.es/Cristalografi
en.html.
The Patterson Function, www.bio.brandeis.edu/classes/archives/biochem102/sftut/frame_patt1.html.
“Phasing_handout1.” Ocw.mit.edu, 2010, Spring, ocw.mit.edu/courses/chemistry/5-069-crystal-structure-analysis-spring-2010/lecture-notes/phasing_handout1.pdf.

ATOM	**x**	**y**	**z**	**sof**	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**	**Ueq**
Ca2	0.0122	0.0085	0.0081	0.50000	0.01088	0.01165	0.00813	0.00000	0.00000	0.00700	0.00962
				0.00000	0.00013	0.00013	0.00012	0.00000	0.00000	0.00010	0.00008
Ca1	0.0126	0.0126	0.0073	0.33333	0.01263	0.01263	0.00733	0.00000	0.00000	0.00632	0.01086
				0.00000	0.00011	0.00011	0.00015	0.00000	0.00000	0.00005	0.00009
P3	0.0074	0.0070	0.0061	0.50000	0.00728	0.00678	0.00698	0.00000	0.00000	0.00394	0.00683
				0.00000	0.00015	0.00015	0.00015	0.00000	0.00000	0.00012	0.00008
F	0.0482	0.0099	0.0099	0.16000	0.00993	0.00993	0.04818	0.00000	0.00000	0.00496	0.02268
				0.00000	0.00054	0.00054	0.00156	0.00000	0.00000	0.00027	0.00049
O1	0.0209	0.0120	0.0081	0.50000	0.00808	0.01118	0.02089	0.00000	0.00000	0.00425	0.01363
				0.00000	0.00043	0.00045	0.00055	0.00000	0.00000	0.00037	0.00021
O2	0.0164	0.0126	0.0066	0.50000	0.01561	0.01183	0.01258	0.00000	0.00000	0.01019	0.01186
				0.00000	0.00048	0.00045	0.00047	0.00000	0.00000	0.00041	0.00019
O3	0.0293	0.0105	0.0073	1.00000	0.02631	0.01324	0.01094	0.00461	0.00743	0.01243	0.01570
				0.00000	0.00042	0.00034	0.00035	0.00028	0.00031	0.00032	0.00017
Cl	0.1499	0.0648	0.0648	0.01333	0.06480	0.06480	0.14990	0.00000	0.00000	0.03240	0.09317
				0.00000	0.01132	0.01132	0.04008	0.00000	0.00000	0.00566	0.01386

Table 4: Above are the calculated interatomic from the direct method. The x,y,z values are principle mean squared atomic displacements

ATOM	**x**	**y**	**z**	**sof**	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**	**Ueq**
Ca1	0.0126	0.0126	0.0073	0.33333	0.01263	0.01263	0.00732	0.00000	0.00000	0.00631	0.01086
				0.00000	0.00011	0.00011	0.00015	0.00000	0.00000	0.00005	0.00009
Ca2	0.0122	0.0085	0.0081	0.50000	0.01088	0.01165	0.00813	0.00000	0.00000	0.00700	0.00961
				0.00000	0.00013	0.00013	0.00012	0.00000	0.00000	0.00010	0.00008
P3	0.0074	0.0070	0.0061	0.50000	0.00619	0.00728	0.00698	0.00000	0.00000	0.00334	0.00682
				0.00000	0.00015	0.00015	0.00015	0.00000	0.00000	0.00012	0.00008
F	0.0482	0.0099	0.0099	0.16000	0.00992	0.00992	0.04819	0.00000	0.00000	0.00496	0.02268
				0.00000	0.00054	0.00054	0.00156	0.00000	0.00000	0.00027	0.00049
O1	0.0209	0.0119	0.0081	0.50000	0.01076	0.00808	0.02088	0.00000	0.00000	0.00382	0.01363
				0.00000	0.00046	0.00043	0.00055	0.00000	0.00000	0.00037	0.00021
O2	0.0164	0.0126	0.0066	0.50000	0.00707	0.01561	0.01258	0.00000	0.00000	0.00543	0.01186
				0.00000	0.00041	0.00048	0.00047	0.00000	0.00000	0.00038	0.00019
O3	0.0293	0.0105	0.0073	1.00000	0.01469	0.02631	0.01094	0.00743	0.00282	0.01388	0.01570
				0.00000	0.00034	0.00042	0.00035	0.00031	0.00028	0.00032	0.00017
Cl	0.1508	0.0648	0.0648	0.01333	0.06478	0.06478	0.15083	0.00000	0.00000	0.03239	0.09347
				0.00000	0.01132	0.01132	0.04040	0.00000	0.00000	0.00566	0.01395

Table 5: Above are the calculated interatomic from the Patterson method. The x,y,z values are principle mean squared atomic displacements. They identical in nearly all cases.

"X-Ray Diffraction." X-Ray Diffraction - an Overview — ScienceDirect Topics, www.sciencedirect.com/topics/m
science/x-ray-diffraction.