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 this crystal is 504.9 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 vice 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.

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

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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.

2.3 Least Squares Method

To calculate the error for each iteration of model improvement, the least squares method is used. The loss function is calculated as the sum of the squared differences of model positions and the measured positions (residuals). The sum of the squared residuals for the x,y,and z positions are written in eq. 8, where n are the total number of atoms considered. x_{calc}, y_{calc}, and z_{calc} are all functions of parameters that can be tweaked between iterations to minimize the loss.

$$s_x = \sum_{i=1}^{n} \left(x_{calc} - x_{model}\right)^2, \; s_y = \sum_{i=1}^{n} \left(y_{calc} - y_{model}\right)^2, \; s_z = \sum_{i=1}^{n} \left(z_{calc} - z_{model}\right)^2 \tag{8}$$

2.4 Bond Valence Sums

After fitting the atomic positions, we can calculate the bond valence sum (BVS) using the interatomic distances from the Patterson fitting. The BVS is the sum of all the bond valences (S_{ij}), where each bond valence depends on its distance from other atoms and two constant parameters, R_0 and B (eq. 2).

$$S_{ij} = exp\left[\frac{(R_0 - R_{ij})}{B}\right] \qquad (9)$$

3 Sample Preparation and Data Collection

First we cleaned a glass coverslip and placed a drop of DI water on it. Then we added 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°.

4 Resulting Structure

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

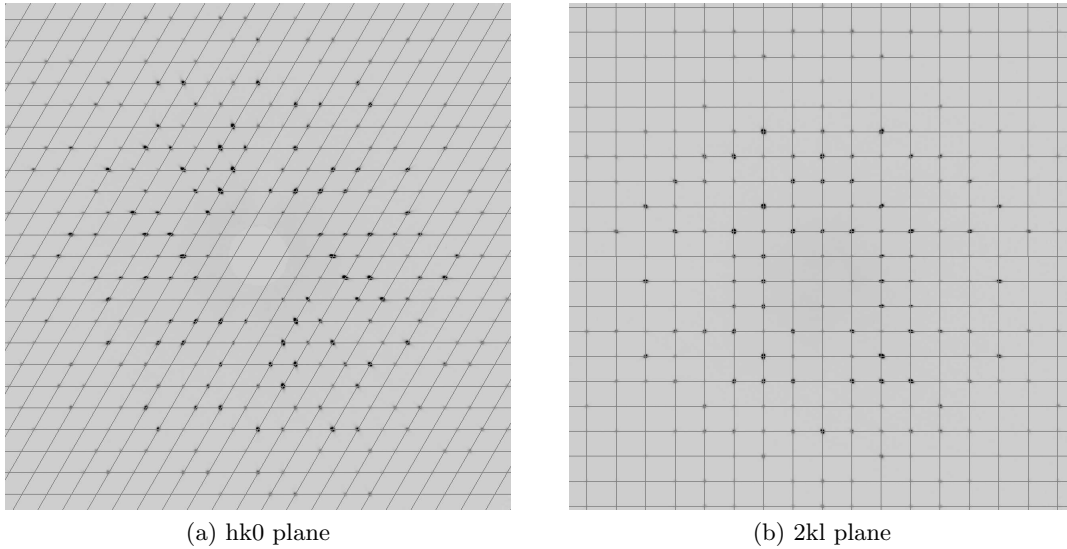(a) hk0 plane (b) 2kl plane

Figure 1: Here are two different hkl planes

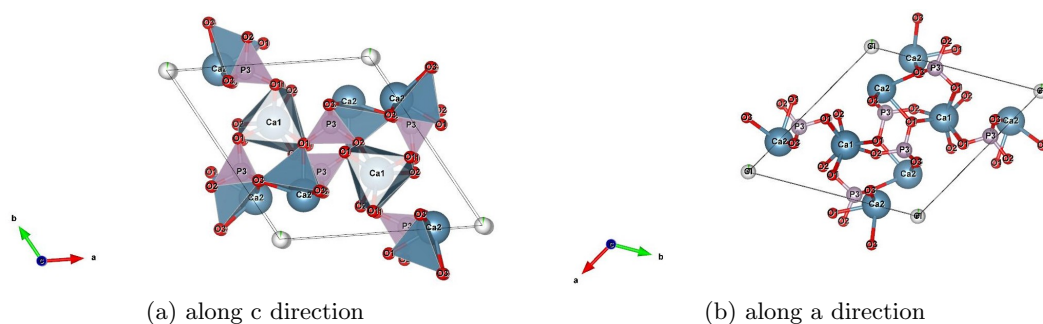(a) along c direction   (b) along a direction

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: Below 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	1.8650	Ca_1	1.8651
Ca_2	2.0275	Ca_2	2.0334
P	4.9791	P	4.9788

ATOM	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
Ca_2	0.0122	0.0085	0.0081	0.50000	0.01088	0.01165	0.00813	0.00000	0.00000	0.00700	0.00962
Ca_2 Errors				0.00000	0.00013	0.00013	0.00012	0.00000	0.00000	0.00010	0.00008
Ca_1	0.0126	0.0126	0.0073	0.33333	0.01263	0.01263	0.00733	0.00000	0.00000	0.00632	0.01086
Ca_1 Errors				0.00000	0.00011	0.00011	0.00015	0.00000	0.00000	0.00005	0.00009
P_3	0.0074	0.0070	0.0061	0.50000	0.00728	0.00678	0.00698	0.00000	0.00000	0.00394	0.00683
P_3 Errors				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
F Errors				0.00000	0.00054	0.00054	0.00156	0.00000	0.00000	0.00027	0.00049
O_1	0.0209	0.0120	0.0081	0.50000	0.00808	0.01118	0.02089	0.00000	0.00000	0.00425	0.01363
0_1 Errors				0.00000	0.00043	0.00045	0.00055	0.00000	0.00000	0.00037	0.00021
O_2	0.0164	0.0126	0.0066	0.50000	0.01561	0.01183	0.01258	0.00000	0.00000	0.01019	0.01186
0_2 Errors				0.00000	0.00048	0.00045	0.00047	0.00000	0.00000	0.00041	0.00019
O_3	0.0293	0.0105	0.0073	1.00000	0.02631	0.01324	0.01094	0.00461	0.00743	0.01243	0.01570
0_3 Errors				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
Cl Errors				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

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

Atom	Wyckoff position	Direct method			Patterson method		
		x	y	z	x	y	z
Ca_1	6h	0.249206	0.242123	0.250000	0.750796	0.757878	0.250000
error		0.00812	0.00000	0.00000	0.00812	0.00000	0.00000
Ca_2	4f	0.666667	0.333333	0.001163	0.333333	0.666667	0.498836
error		0.00731	0.00000	0.00000	0.00731	0.00000	0.00000
P	6h	0.601526	0.0.630994	0.250000	0.970535	0.601526	0.250000
error		0.00696	0.00000	0.00000	0.00696	0.00000	0.00000
F	2a	0.000000	0.000000	0.250000	1.000000	1.000000	0.250000
error		0.04734	0.00000	0.00000	0.04734	0.00000	0.00000
O_1	6h	0.412079	0.533297	0.250000	1.157439	0.672834	0.250000
error		0.02086	0.00000	0.00000	0.01258	0.00000	0.00000
O_2	6h	0.672833	0.515391	0.250000	0.878784	0.412081	0.250000
error		0.01258	0.00000	0.00000	0.02085	0.00000	0.00000
O_3	12i	0.658210	0.742762	0.070452	0.915447	0.658210	0.070446
error		0.01093	0.00460	0.00742	0.01092	0.00741	0.00282
Cl	2a	0.000000	0.000000	0.126183	1.000000	1.000000	0.125501
error		0.13024	0.00000	0.00000	1.000000	1.000000	0.125501

ATOM	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
Ca_1	0.0126	0.0126	0.0073	0.33333	0.01263	0.01263	0.00732	0.00000	0.00000	0.00631	0.01086
Ca_1 Errors				0.00000	0.00011	0.00011	0.00015	0.00731	0.00000	0.00005	0.00009
Ca_2	0.0122	0.0085	0.0081	0.50000	0.01088	0.01165	0.00813	0.00000	0.00000	0.00700	0.00961
Ca_2 Errors				0.00000	0.00013	0.00013	0.00012	0.00000	0.00000	0.00010	0.00008
P_3	0.0074	0.0070	0.0061	0.50000	0.00619	0.00728	0.00698	0.00000	0.00000	0.00334	0.00682
P_3 Errors				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
F Errors				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
O_1 Errors				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
O_2 Errors				0.00000	0.00041	0.00048	0.00047	0.00000	0.00000	0.00038	0.00019
O_3	0.0293	0.0105	0.0073	1.00000	0.01469	0.02631	0.01094	0.00743	0.00282	0.01388	0.01570
O_3 Errors				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
Cl Errors				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.

5 Discussion

Figure 1 shows excellent agreement with the determined space group, since both the bond angles angles and predicted systematic extinction are seen. These extinctions are a result of the 6_3 screw axis. Additionally, the spots in figure 1 are well resolved and clear. The calculated $\langle |E_{\mathrm{hkl}}^2 - 1| \rangle$ value of 0.974 is close to the predicted value of 0.968 for centrosymmetric structures (see equation 6). The direct method and Patterson methods both produce very similar results, another positive sign for an accurately determined structure. Because there is not a single particularly large atom present in the material, the direct determination method may be better.Both the direct and Patterson methods had a small R1 value of just 0.0202 (smaller indicates higher data quality).

References

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