[1] Barium titanate

Barium titanate $\text{BaTiO}_3$ has a phase with a structure in which the Barium (Ba; $137 \text{ g mol}^{-1}$) atoms are at the corners of a cube with a titanium (Ti; $48 \text{ g mol}^{-1}$) atom at the center and oxygen (O; $16 \text{ g mol}^{-1}$) atoms at the center of each face of the cube. In this phase, barium titanate has a mass density $\rho = 6.02 \text{ g cm}^{-3}$. Barium titanate power is exposed to X-rays with a wavelength $\lambda = 0.154 \text{ nm}$ in a Debye-Scherrer experiment. The Avogadro number is $N = 6.02 \times 10^{23} \text{ mol}^{-1}$

(a) Describe the structure, specifying the lattice and basis and calculate the lattice constant.

The lattice of this crystal is simple cubic with the following basis

\[
\begin{align*}
\text{Ba} : (0,0,0) \quad &\text{Ti} : a \left( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right) \\
\text{O} : &\left( \frac{a}{2}, 1, 0 \right) \quad \text{O} : \left( \frac{a}{2}, 1, 1 \right) \quad \text{O} : \left( 1, 1, 0 \right)
\end{align*}
\]

where $a$ is the simple cubic lattice constant & we are using the system of axes directed by $\hat{z}, \hat{y}, \hat{z}$ along the corner of the cube around.

The mass density $\rho$ of the crystal is the mass of atoms in the unit cell divided by the volume of the unit cell $\rho = \frac{\sum M_i}{a^3}$, so

\[
a = \left( \frac{137 + 48 + 3 \times 16}{6.02 \times 10^{23} \times 6.02} \right)^{1/3} = 4 \times 10^{-8} \text{ cm} = 0.4 \text{ nm} \quad a = 0.4 \text{ nm}
\]

(b) Calculate the Bragg deflection angles for the first four peaks that appear in the Debye-Scherrer experiment.

\[\theta \text{ of Bragg's condition} \quad 2d \sin \theta = n \lambda \quad \text{where} \quad d \text{ is the distance between lattice planes, } \theta \text{ is the half deflection angle and } n \text{ is the interference order, which we can set to } n = 1 \text{ as long as we are interested by the smallest deflection angle, } 2 \theta\]

\[\text{A family of lattice } \lambda \text{ planes can be identified by a reciprocal } \vec{K} \text{ such that } d = \frac{2\pi}{|\vec{K}|} \quad \text{so} \quad \theta = \sin^{-1} \left( \frac{\lambda |\vec{K}|}{4\pi} \right)\]

\[\text{With a cubic lattice, } |\vec{K}| = \frac{2\pi}{a} \sqrt{k^2 + l^2 + m^2} \quad \text{with } (k, l, m) \in \mathbb{Z}^3\]

\[
\begin{array}{|c|c|c|}
\hline
k, l, m & \sqrt{k^2 + l^2 + m^2} & \theta (\degree) & 2\theta (\degree) \\
\hline
1, 0, 0 & 1 & 11.099 & 22.198 \\
1, 1, 0 & \sqrt{2} & 15.797 & 31.594 \\
1, 1, 1 & \sqrt{3} & 19.476 & 38.953 \\
2, 0, 0 & 2 & 22.644 & 45.288 \\
\hline
\end{array}
\]
(c) Assuming the atomic form factors are constant with $f_{Ba} = 7f_O$ and $f_{Ti} = 3f_O$, establish the intensity relationship between the first four peaks.

- The intensity of each Bragg peak $I_{klm} \propto M_{klm} |S_{klm}|^2$ where $M_{klm}$ is the symmetry multiplicity factor, we need to establish for each $(klm)$ and
  
  $S_{klm} = \sum_{j=1}^{N} f_j(k) e^{iK \cdot \vec{r}_j}$

  where $\vec{r}_j$ is the position of the $j^{th}$ atom in the unit cell & $K = \frac{2\pi}{a} (k \hat{x} + l \hat{y} + m \hat{z})$

  $S_{klm} = f_{Ba} + f_{Ti} e^{i\pi(k+l+m)} + f_O \left( e^{i\pi(l+m)} + e^{i\pi(k+m)} + e^{i\pi(k+l)} \right)$

- Using $f_{Ba} = 7f_O$ & $f_{Ti} = 3f_O$,

  $S_{klm} = f_O \left( 1 + 3 e^{i\pi(k+l+m)} + e^{i\pi(l+m)} + e^{i\pi(k+m)} + e^{i\pi(k+l)} \right)$

| $(k,l,m)$ | $M_{klm}$ | $S_{klm}/f_O$ | $\frac{I_{klm}}{I_{iso}} = \frac{M_{klm} |S_{klm}|^2}{M_{iso} |S_{iso}|^2}$ |
|-----------|------------|----------------|---------------------------------|
| $(1,0,0)$ | 6          | 3              | 1.0                             |
| $(1,1,0)$ | 12         | 9              | 18                              |
| $(1,1,1)$ | 8          | 7              | 7.26                            |
| $(2,0,0)$ | 6          | 13             | 18.7                            |

The data may look like on the following graph.
Hexagonal close pack again!

The primitive vectors for a hexagonal close pack structure can be chosen as follows: \( \mathbf{a}_1 = \frac{\sqrt{3}}{2} a \mathbf{\hat{x}} + \frac{1}{2} a \mathbf{\hat{y}} \); \( \mathbf{a}_2 = -\frac{\sqrt{3}}{2} a \mathbf{\hat{x}} + \frac{1}{2} a \mathbf{\hat{y}} \) and \( \mathbf{a}_3 = 2 \sqrt{3} a \mathbf{\hat{z}} \) and, with this choice, the two atoms in the primitive unit cell are located in \((0,0,0)\) and \((\frac{\sqrt{3}}{6} a, \frac{1}{2} a, \sqrt{3} a)\). Assuming all the atoms are identical with a unit atomic structure factor \( S_{\text{Atomic}} = 1 \), calculate the magnitude squared \( |S_{klm}| \) of the unit cell structure factor for \((h,k,l)\) taking the values \{(1,0,0); (1,0,1); (1,0,2); (1,0,3); (0,0,1); (0,0,2); (1,1,0); (1,1,1); (1,1,2)\}.

In previous homework we calculated the simple hexagonal reciprocal lattice primitive vectors: \( \mathbf{b}_1 = \frac{2 \pi}{a} \left( \frac{1}{\sqrt{3}} \mathbf{\hat{x}} + \mathbf{\hat{y}} \right), \mathbf{b}_2 = \frac{2 \pi}{a} \left( -\frac{1}{\sqrt{3}} \mathbf{\hat{x}} + \mathbf{\hat{y}} \right) \) \& \( \mathbf{b}_3 = \frac{\pi}{a} \sqrt{3} \mathbf{\hat{z}} \).

Any reciprocal vector \( \mathbf{K} = k \mathbf{b}_1 + l \mathbf{b}_2 + m \mathbf{b}_3 \) and, the basis form factor is \( S_{klm} = \sum_{j=1}^{N} S_{\text{Atom}j} \epsilon_{ikl} \mathbf{K} \cdot \mathbf{\alpha}_j \), as in the previous exercise. In our specific case:

\[
S_{klm} = \sum_{j=1}^{N} S_{\text{Atom}j} \epsilon_{ikl} \mathbf{K} \cdot \mathbf{\alpha}_j \]

with \( S_{\text{Atom}j} = 1 \) we get \( S_{klm} = 1 + \epsilon_{ikl} \mathbf{K} \cdot \mathbf{\alpha} \) with \( \mathbf{\alpha} = a \left( \frac{\sqrt{3}}{6} \mathbf{\hat{x}} + \frac{1}{2} \mathbf{\hat{y}} + \sqrt{3} \mathbf{\hat{z}} \right) \)

\[
\begin{align*}
\mathbf{b}_1 \cdot \mathbf{\alpha} &= 2 \pi \left( \frac{1}{\sqrt{3}} + \frac{1}{2} \right) = \frac{4 \pi}{3} , \\
\mathbf{b}_2 \cdot \mathbf{\alpha} &= 2 \pi \left( -\frac{1}{6} + \frac{1}{2} \right) = \frac{2 \pi}{3} , \\
\mathbf{b}_3 \cdot \mathbf{\alpha} &= \pi \\
\end{align*}
\]

So \( \mathbf{K} \cdot \mathbf{\alpha} = \pi \left( \frac{4}{3} k + \frac{2}{3} l + m \right) \) and

\[
S_{klm} = 1 + \epsilon_{ikl} \frac{2 \pi}{3} (2k+l)
\]

Using this expression we can build the following table.

| \(k,l,m\) | \(S_{klm}\) | \(|S_{klm}|^2\) |
|-----------|-------------|----------------|
| 1 0 0     | 1 - \(\frac{1}{2} + i \frac{\sqrt{3}}{2}\) | 1              |
| 1 0 1     | 1 + \(\frac{1}{2} - i \frac{\sqrt{3}}{2}\) | 3              |
| 1 0 2     | 1 - \(\frac{1}{2} + i \frac{\sqrt{3}}{2}\) | 1              |
| 1 0 3     | 1 + \(\frac{1}{2} - i \frac{\sqrt{3}}{2}\) | 3              |
| 0 0 1     | 0           | 0              |
| 0 0 2     | 2           | 4              |
| 1 1 0     | 2           | 4              |
| 1 1 1     | 0           | 0              |
| 1 1 2     | 2           | 4              |

In order to estimate the relative intensity of the Bragg peaks, we would have to also calculate the multiplicity of the plane families....
Atomic X-ray form factor

As a first step toward including the atomic form factor for X-ray diffraction, one can consider the Z electrons of an atom to be uniformly distributed in a sphere of radius $r_0$. Show that the form factor of a uniform sphere of radius $r_0$ can be written $f(G) = 3Z \frac{\sin(x_0) - x_0 \cos(x_0)}{x_0^3}$ with $x_0 = |Gr_0|$.

\(\diamond\) We need to calculate $f(G) = \int dr^3 \rho(r) e^{iG \cdot r}$ with $\rho(r < r_0) = \rho_0$, $\rho(r > r_0) = 0$.

\(\diamond\) We can use the direction of $G$ as a "\(\hat{z}\) axis" to define a spherical coordinate system $(r, \theta, \phi)$ with which:

$$f(G) = \int_0^{\infty} r^2 \sin \theta \, dr \, \int_0^{\pi} \sin \theta \, d\theta \, \int_0^{2\pi} e^{iG \cdot r} \, d\phi \, e^{i|G|r \cos \theta}.$$

Integration along $\phi$ amounts to a $2\pi$ factor & we can introduce $M = \cos \theta \to dM = -\sin \theta \, d\theta$:

$$f(G) = 2\pi \rho_0 \int_0^{r_0} r^2 \, dr \int_{-1}^{1} \sin \theta \, dM \frac{e^{i|G|r}}{i|G|r} = 2\pi \rho_0 \int_0^{r_0} r^2 \, dr \left( \frac{e^{i|G|r} - e^{-i|G|r}}{i|G|r} \right).$$

$$f(G) = \frac{4\pi \rho_0}{|G|^3} \int_0^{r_0} |G|r |G| \, dr \sin (|G|r)$$

with $x = |G|r$ & $x_0 = |G|r_0$.

$$f(G) = \frac{4\pi \rho_0}{|G|^3} \int_0^{x_0} dx \, x \sin x = \frac{4\pi \rho_0}{|G|^3} \left[ -x \cos x \bigg|_0^{x_0} + \int_0^{x_0} \cos x \, dx \right].$$

$$f(G) = \frac{4\pi \rho_0}{|G|^3} \left( \sin x_0 - x_0 \cos x_0 \right).$$

\(\diamond\) Considering $\rho_0 = \frac{3Z}{4\pi r_0^3}$, we obtain $f(G) = 3 \frac{Z}{x_0^3} \left( \sin x_0 - x_0 \cos x_0 \right)$. 
