CH3052 Material Science Assignment-1

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CH18B020

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Exercise 1

Part a) Coordination Number

The coordination number of the atoms was found manually by viewing the CIF file on Vesta.

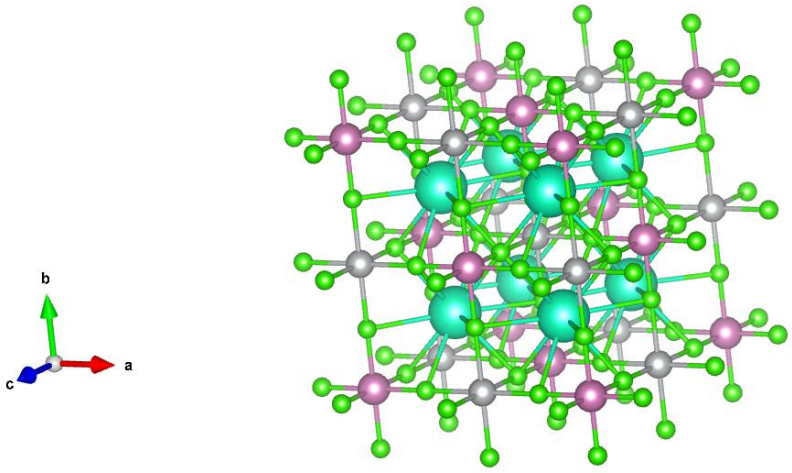

Figure 1: Structure Visualised in Vesta

1. Cs: 12
2. Ag: 6
3. In: 6

Part b) Bond Lengths

The bond lengths were found using the bond length operator and was found to be:

1. Cs-Cl: 3.707 Å
2. Ag-Cl: 2.733 Å
3. In-Cl: 2.507 Å

All bond lengths of a given cation were found to be the same

Part c) Hide bonds greater than 3Å

The Cs-Cl bond were greater than 3Å. Those were removed and the resulting structure is as given below.

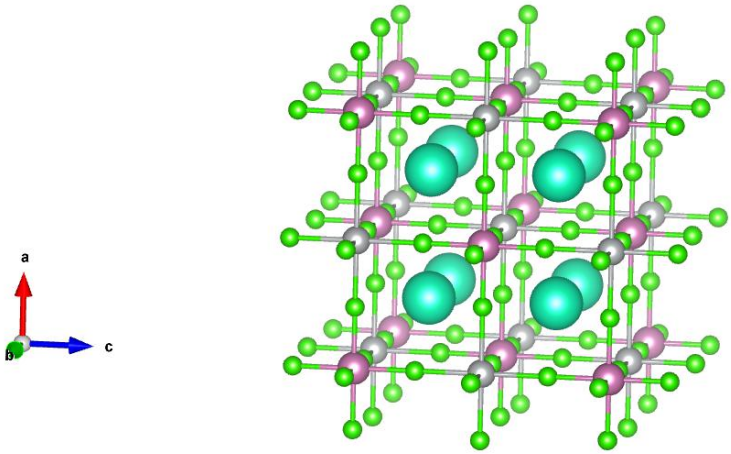

Figure 2: Longer Bonds Removed

Part d) Polyhedral Mode

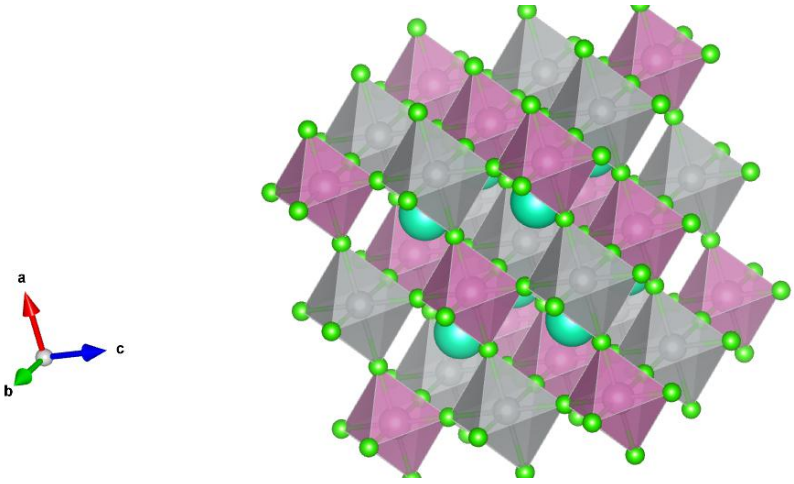

Figure 3: Polyhedral Mode

Purple octahedra are constructed with In (Indium) atom as centre and grey octahedra are constructed with Ag (Silver) atom as centre

Part e) Pore Visualisation

Cs atoms are hidden from the above structure

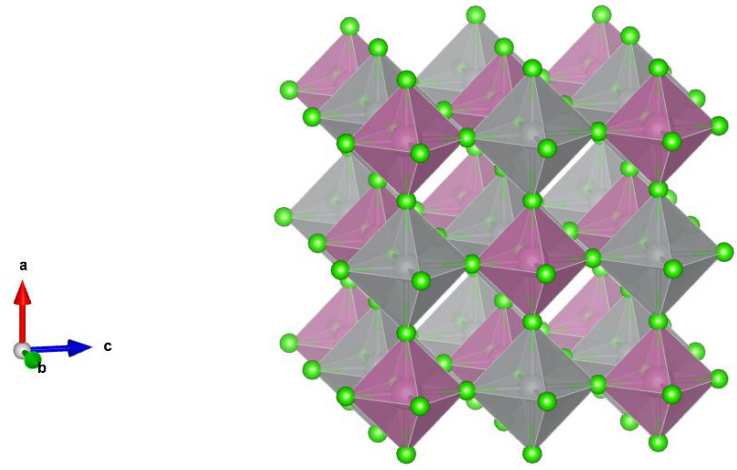

Figure 4: Structure obtained after hiding the Cs atoms

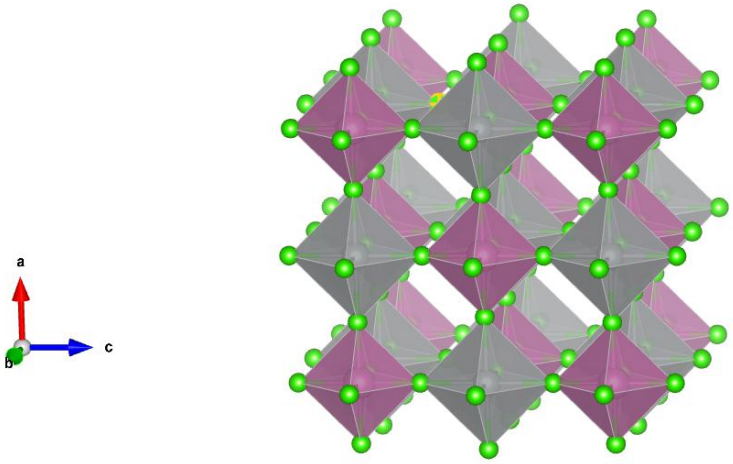

Figure 5: Structure obtained after hiding the Cs atoms; with the narrow pores visible

Part f) Unit Cell & Cation locations

After hiding the bonds and polyhedra we obtain figure 6. These are the coordinates of cations:

1. Locations of **Ag** atoms (**13 atoms** in total displayed; 12 present in **edge centres** and 1 present in **body centre**)
   (a) (10.48059, 0.00000, 5.24030)
   (b) (0.00000, 0.00000, 5.24030)
   (c) (0.00000, 10.48059, 5.24030)
   (d) (10.48059, 10.48059, 5.24030)
   (e) (0.0000, 5.2403, 0.00000)

(f) (0.0000, 5.2403, 10.48059)

(g) (10.48059, 5.24030, 10.48059)

(h) (10.48059, 5.24030, 0.0000)

(i) (5.24030, 0.00000, 10.48059)

(j) (5.24030, 10.48059, 0.0000)

(k) (5.24030, 0.00000, 0.00000)

(l) (5.24030, 10.48059, 10.48059)

(m) (5.24030, 5.24030, 5.24030)

2. Locations of **In** atoms (**16 atoms** in total displayed; 6 present in **face centres** and 8 in **corners**)

(a) (0,0,0)

(b) (10.48059, 0.00000, 0.00000)

(c) (5.24030, 5.24030, 0.00000)

(d) (5.24030, 10.48059, 5.24030)

(e) (10.48059, 5.24030, 5.24030)

(f) (10.48059, 0.00000, 10.48059)

(g) (10.48059, 10.48059, 0.00000)

(h) (10.48059, 10.48059, 10.48059)

(i) (10.48059, 0.00000, 10.48059)

(j) (5.24030, 5.24030, 10.48059)

(k) (0.00000, 0.00000, 10.48059)

(l) (0.00000, 10.48059, 10.48059)

(m) (0.00000, 5.24030, 5.24030)

(n) (0.00000, 10.48059, 0.00000)

(o) (5.24030, 10.48059, 5.24030)

(p) (5.24030, 0.00000, 5.24030)

3. Locations of **Cs** atoms (**8 atoms** in total displayed; All of them present in **tetrahedral voids**)

(a) (2.62015, 2.62015, 2.62015)

(b) (7.86044, 2.62015, 2.62015)

(c) (2.62015, 7.86044, 2.62015)

(d) (2.62015, 2.62015, 7.86044)

(e) (2.62015, 7.86044, 7.86044)

(f) (7.86044, 7.86044, 2.62015)

(g) (7.86044, 2.62015, 7.86044)

(h) (7.86044, 7.86044, 7.86044)

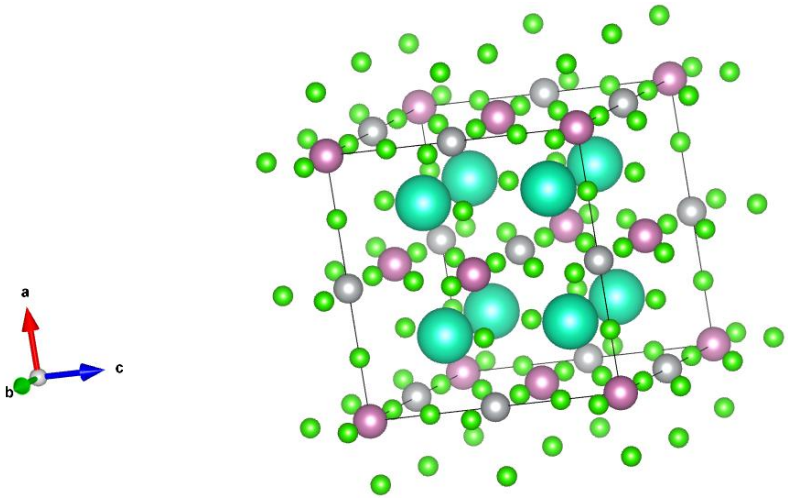

Figure 6: Visualising the unit cell

Effective number of Ag atoms = $12 \cdot \frac{1}{4} + 1 = 4$
Effective number of Cs atoms = $8 \cdot 1 = 8$
Effective number of In atoms = $8 \cdot \frac{1}{8} + 6 \cdot \frac{1}{6} = 4$
Effective number of Cl atoms = $48 \cdot \frac{1}{4} + 12 \cdot \frac{1}{2} = 24$
(48 atoms on edges in the middle of edge centre and corner. 12 atoms on faces in the middle of face centre and an edge centre)

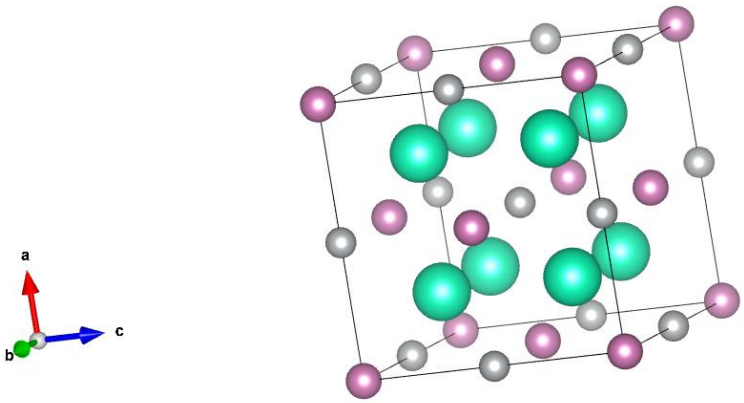

Figure 7: Visualising the unit cell with just the cations

Part g) Miller Planes

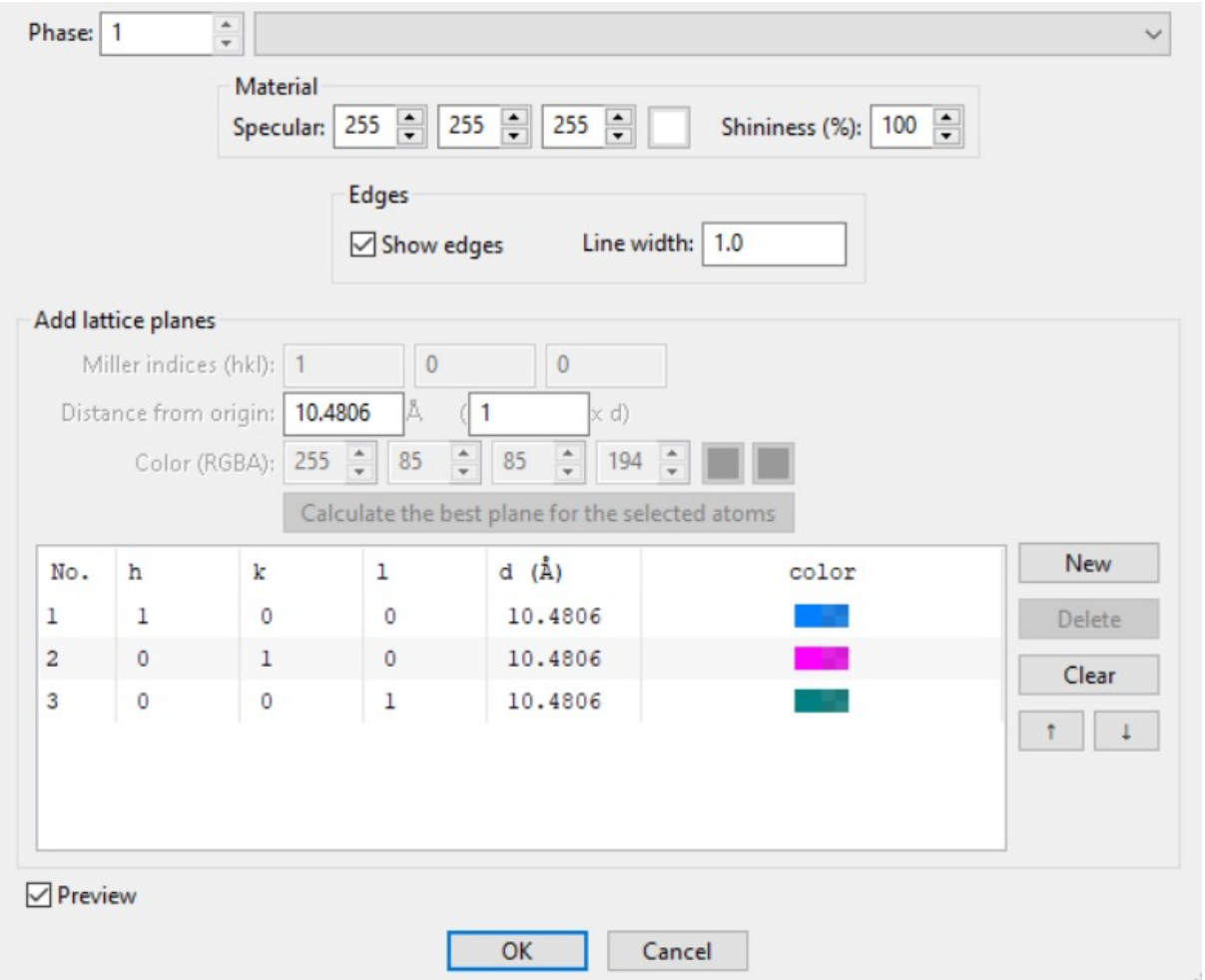

Figure 8: Generating the planes in Vesta

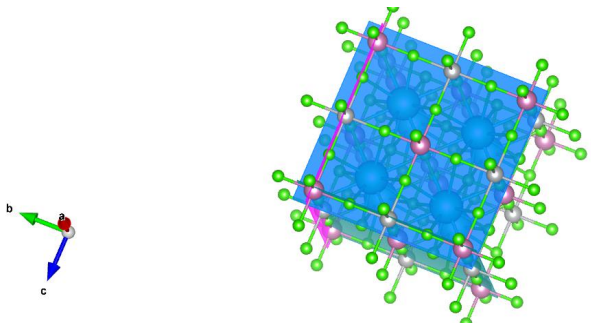

Figure 9: Plane (100)

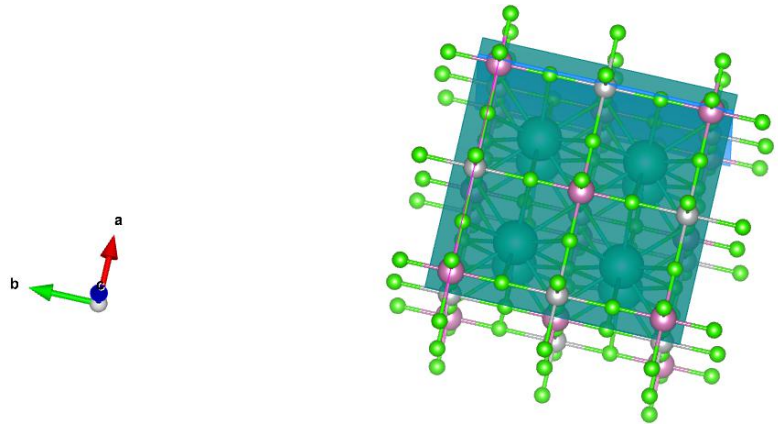

Figure 10: Plane (001)

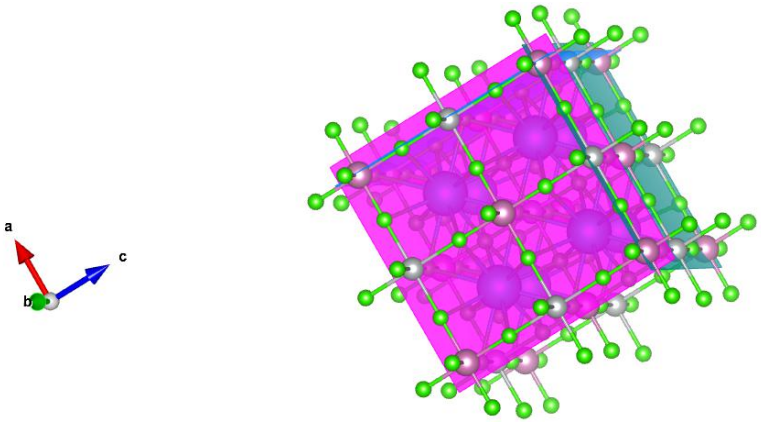

Figure 11: Plane (010)

Yes, all planes have the **same atom composition**: In in corners and centre. Silver in edge centres. Chlorine atoms in between In and Ag parallel to edges. All the planes belong to the **same family**.

Part h) Family of Planes

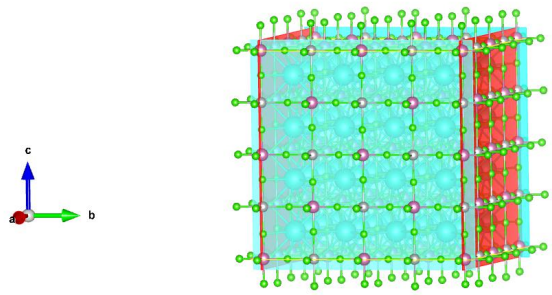

Figure 12: (100) Plane

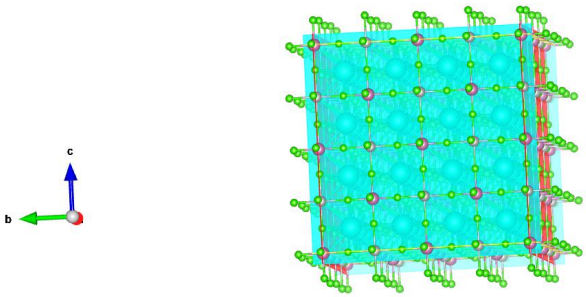

Figure 13: (-100) Plane

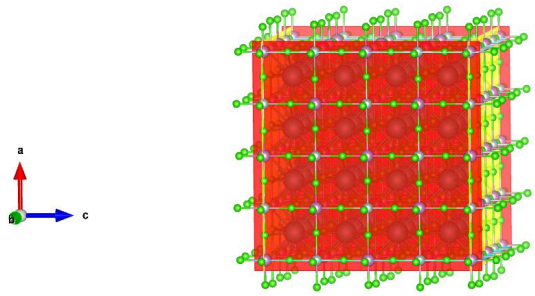

Figure 14: (010) Plane

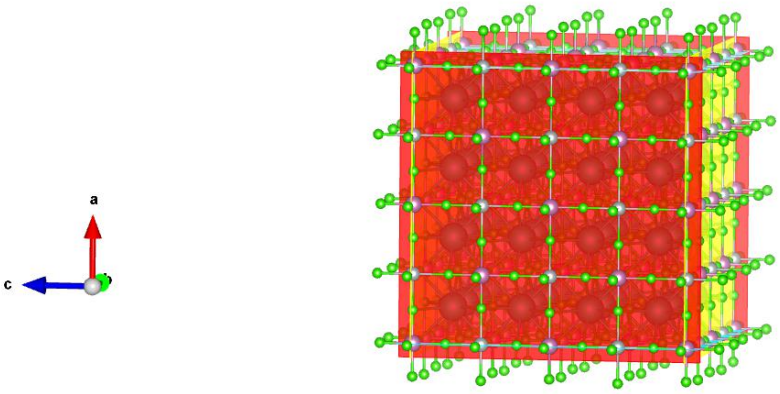

Figure 15: (0 -1 0) Plane

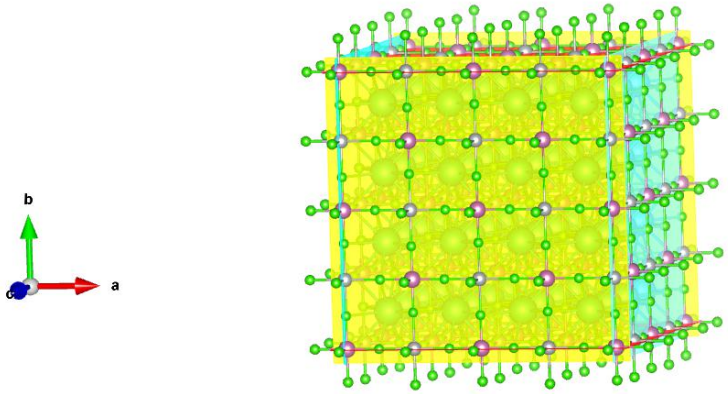

Figure 16: (001) Plane

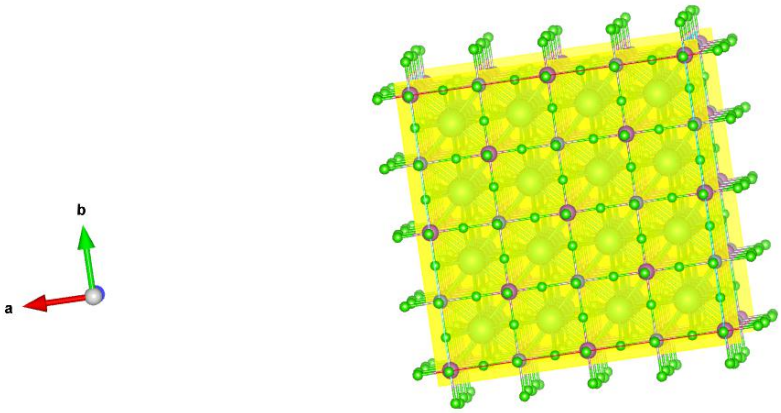

Figure 17: (0 0 -1) Plane

Part i) Comparing (101) and (100) planes

100 Plane (Refer figure 18)
Bond Lengths:

1. In-Cl: 2.507Å
2. Ag-Cl: 2.733Å

Bond Angles:

1. Cl-Ag-Cl: 90°
2. Cl-In-Cl: 90°

101 Plane (Refer figure 19)
Bond Lengths:

1. In-Cl: 2.507Å
2. Ag-Cl: 2.733Å
3. Cs-Cl: 3.7072Å

Bond Angles:

1. Cl-Ag-Cl: 90°
2. Cl-In-Cl: 90°
3. Cl-Cs-Cl: 62.84°

Between the same set of atoms, bond angles and bond lengths remain the same across planes.

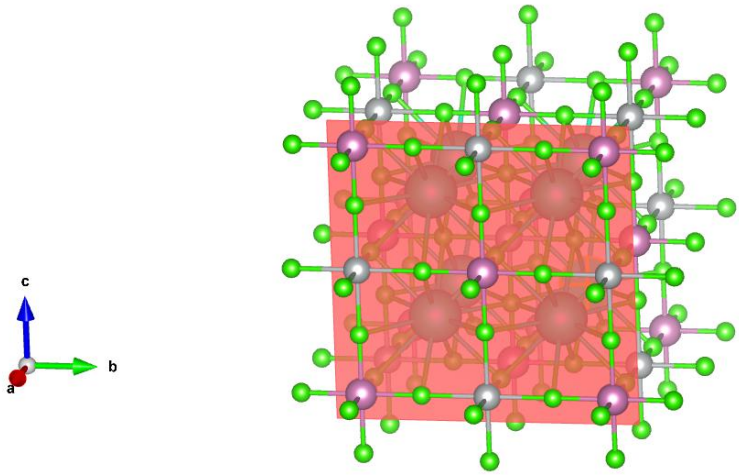

Figure 18: Atoms on 100 Plane

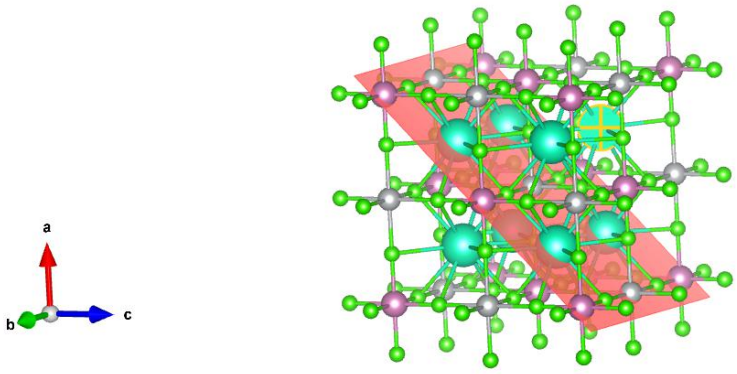

Figure 19: Atoms on 101 Plane

Exercise 2

Part a)

Given below is an extract of the lines mentioning the cell parameters in the CIF file:

```
_cell_length_a    10.480593(54)
_cell_length_b    10.480593(54)
_cell_length_c    10.480593(54)
_cell_angle_alpha  90
_cell_angle_beta   90
_cell_angle_gamma  90
_cell_volume  1151.218(18)
```

From the above lines in the *.CIF* file we find that the parameter values are $a = b = c = 10.4806$Å and $\alpha = \beta = \gamma = 90^{\circ}$
Parameters as shown in Vesta:

Lattice parameters

a	b	c	alpha	beta	gamma
10.48059	10.48059	10.48059	90.0000	90.0000	90.0000

Figure 20: Screenshot of parameters displayed in Vesta

Obviously, since Vesta takes the parameters from the CIF file, the parameters taken in both places match perfectly.
Space Group: Fm-3m **Space Group Number: 225**
Explanation:

1. **F**: It gives the crystal system and centering. The structure is **Face Centred Cubic**

2. The first **m** denotes that there is mirror symmetry with mirror placed along a-axis.
3. **-3** denotes that there is an inversion symmetry and a C_3 rotational symmetry with respect to b-axis.
4. The final **m** denotes that there is a mirror symmetry with mirror along c-axis

Part b) Symmetry Operations

Space Group Number was found to be **225** from this link.
Space Group Diagram was obtained in the following link.

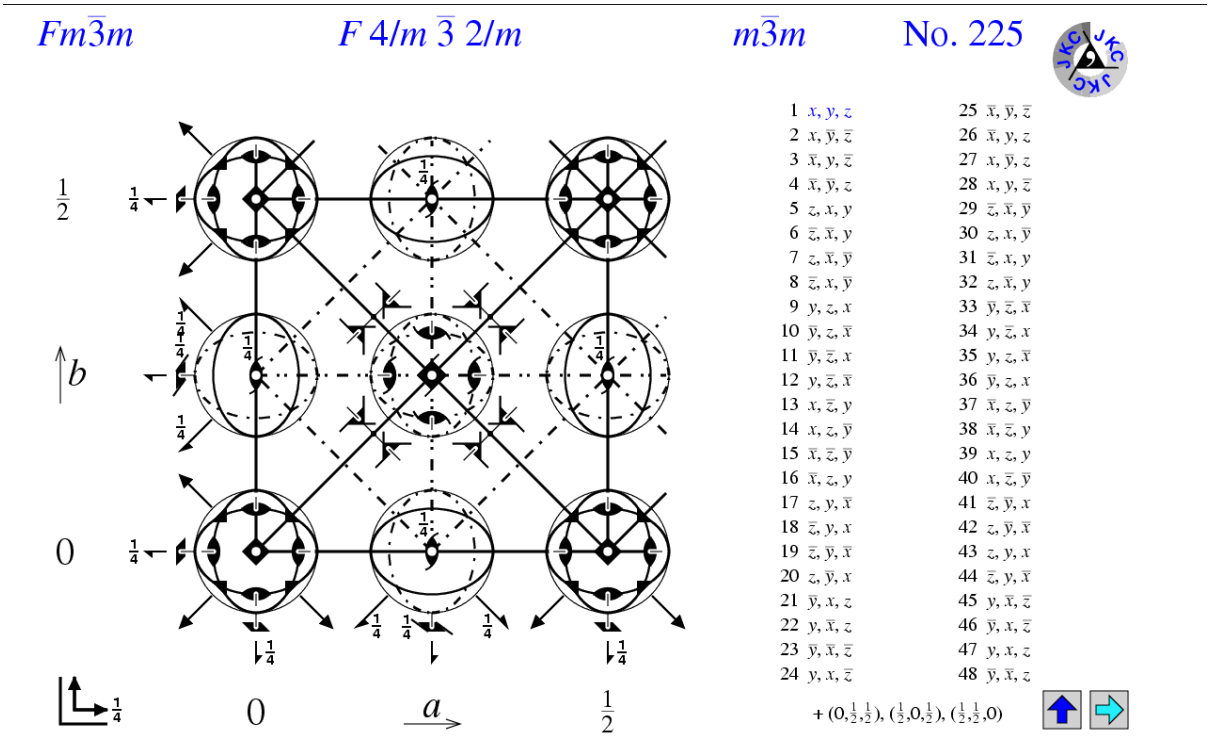

Figure 21: Space group diagram of $Cs_2AgInCl_6$

We find that the crystal has the following symmetry operations:

1. 3_1 screw axis inclined to plane at an angle of 54.736°.
2. 3_2 screw axis inclined to plane at an angle of 54.736°.
3. 2_1 screw axis perpendicular to the plane of the screen with inversion on the axis. The inversion centre lies at a height of 1/4 lattice units.
4. 2_1 screw axis inclined to the plane at an angle of 45°
5. 2_1 screw axis parallel to the plane
6. Glide plane along the diagonals.
7. 4_2 screw axis perpendicular to the plane with centre of inversion on the axis.
8. 4_2 screw axis along '-a' and '-b' directions(parallel to plane), with height of the axis of rotation above the XY plane at $\frac{1}{4}$.

9. C_4 symmetry with respect to axis perpendicular to the plane with a centre of inversion on the axis.
10. C_4 symmetry with respect to axis along '-a' and '-b' directions.(parallel to plane)
11. C_2 symmetry with respect to axes along and opposite to 'a' and 'b' directions. (parallel to the plane)
12. Diagonal planes:
    (a) Inclined at 45° to the plane.
    (b) The dashed-dotted line (which bisects the -YZ axes) indicates a glide direction simultaneously along X and -YZ (look at the spheres in edge centres)
    (c) The thick solid line shows a mirror plane bisecting the YZ axes, i.e. with its normal parallel to -YZ. (look at the spheres in corners)

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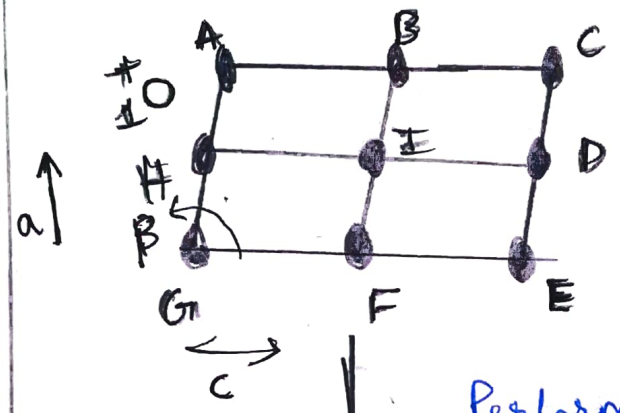
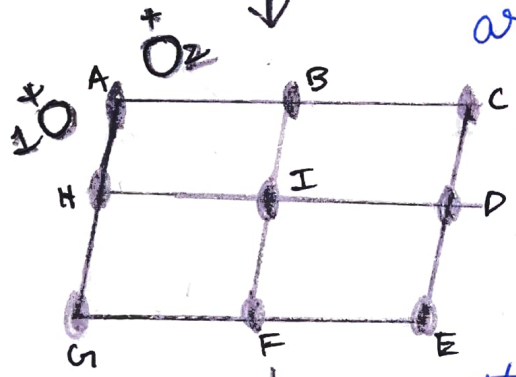
(3)



● indicates C_2 symmetry

Perform C_2 symmetry operation around A.

We obtain atom '2'.



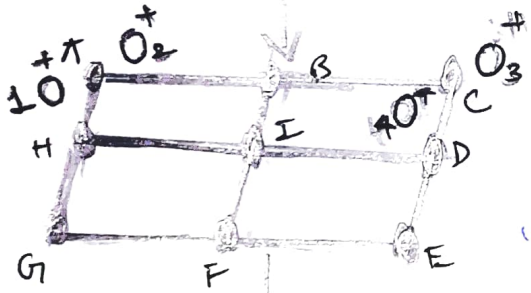
Perform C_2 symmetry operation around 'B' for atoms 1 & 2.

We obtain atoms 3 and 4.

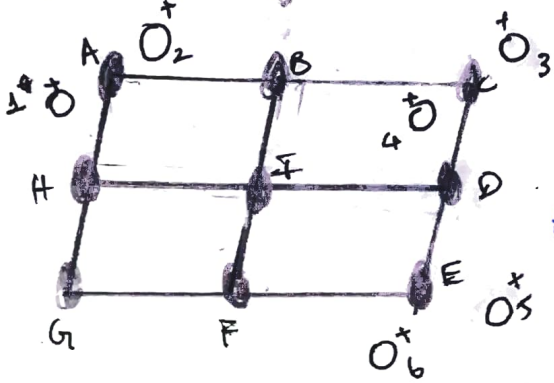
'1' corresponds to '3'

'2' corresponds to '4'

Also C_2 symmetry at C is automatically satisfied by '3' and '4'



Perform C_2 symmetry for 3 and 4 about D.



We obtain atoms 5 and 6.

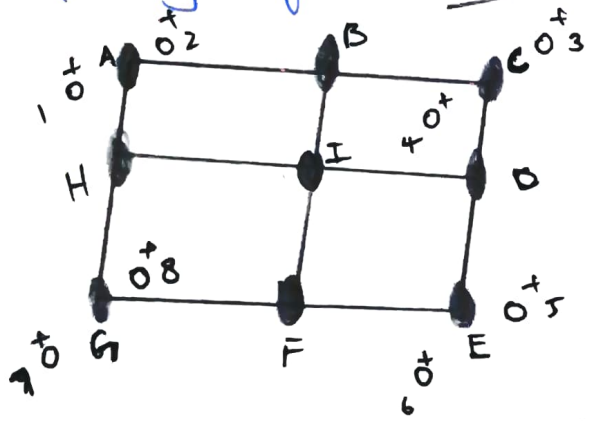
Atom '3' corresponds to '6'

Atom '4' corresponds to '5'.

Further atoms '5' and '6' exhibit C_2 symmetry about E. They also automatically satisfy C_2 Symmetry about I with '1' and '2'.

'1' → '6' & '2' corresponds to '5'.

Finally after a C_2 operation about F,



We generate atoms 7 and 8.

Atom 5 corresponds to 7

Atom 6 corresponds to 8.

Further, 7 and 8 satisfy C_2 operation about G7.

(7, 8) and (1, 2) satisfy C_2 operation about H.

1 corresponds to 8 and 2 corresponds to 7.

And also atoms (3, 4), (7, 8) satisfy C_2 symmetry about I.

7 corresponds to 3, and 8 corresponds to 4.

∴ Using the given symmetry operations we have generated 8 atoms!

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CH3052 Assignment-1

Question-4: X-Ray Diffraction

a) XRD simulation in Vesta

Chosen wavelengths (obtained from the CIF file)

```
12   _diffrn_radiation_wavelength
13 ▼ _diffrn_radiation_wavelength_wt
14    1.5406    1.0000
15    1.5443    0.5000
```

Figure 1: Extract of the CIF file displaying the wavelengths

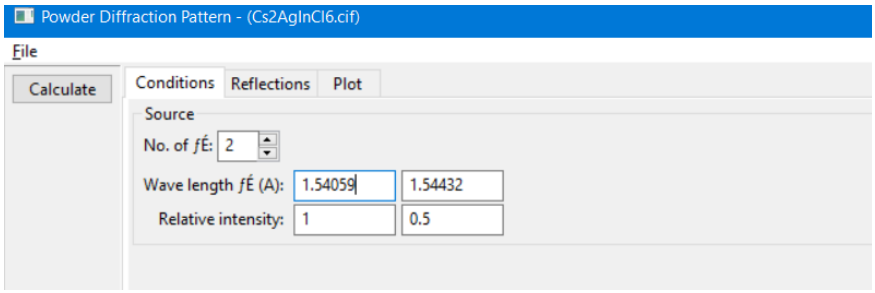

Figure 2: Applying the appropriate wavelengths in Vesta

XRD pattern was generated, and the generated data was exported to an excel file.

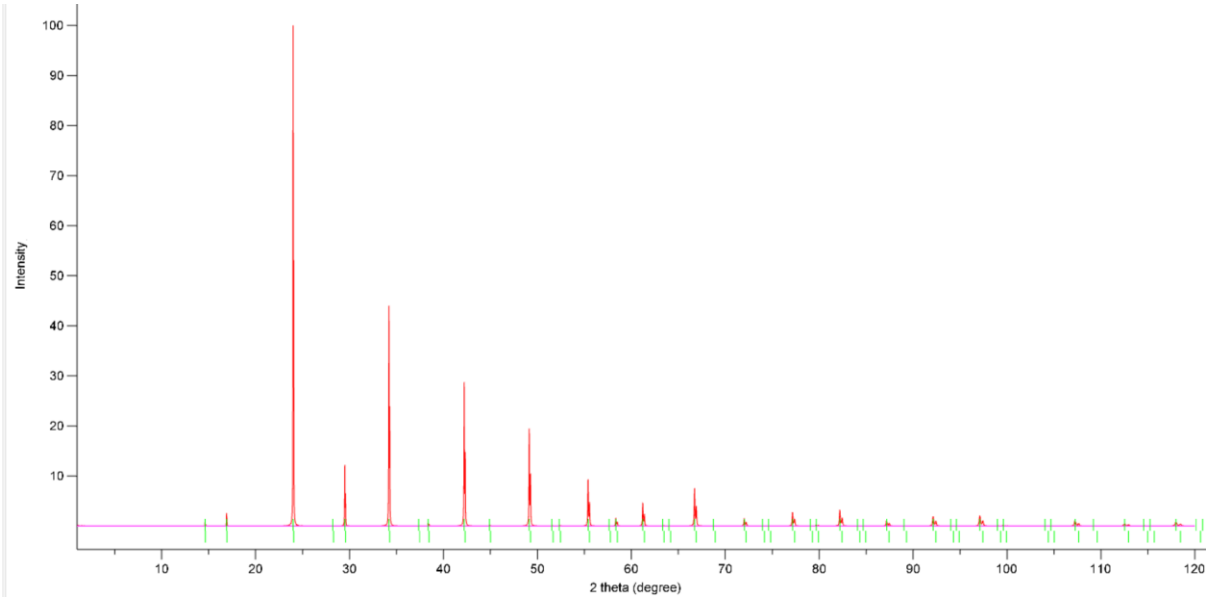

Figure 3: XRD Pattern of $Cs_2AgInCl_6$

Now, from the excel file and with the help of the graph, I identified the peaks and noted down their 2θ values.

We can then get (from Bragg's law): $d = \frac{\lambda}{2 \sin \theta}$

After getting d,

1) For cubic systems: $\frac{a^2}{d_{hkl}^2} = h^2 + k^2 + l^2$
2) Allowed transitions for F type cubic lattices: h + k + l is even.

Using the above rules I found hkl corresponding to the peaks.

I	2θ	dmanual	d_vesta	a^2/d^2	h	k	l		
100	23.99648	3.705474	3.705449	7.999889	2	2	0		
13.27913	29.50001	3.025506	3.025487	11.99984	2	2	2		
54.00956	34.19386	2.620165	2.620148	15.99979	4	0	0		
40.2921	42.20796	2.139356	2.139342	23.99967	4	2	2		
31.78633	49.1348	1.852736	1.852725	31.99957	4	4	0		
16.66272	55.39942	1.657138	1.657127	39.99946	6	2	0		
3.06465	58.35617	1.580019	1.580009	43.9994	6	2	2		
λ	**1.5406**								
a	**10.48059**								
	3.141593								
Comment: Note that for hkl, the entire family of planes will obey that expression and will have that distance									
Comment: Results Agree with Vesta!									

Table 4.1: Table used to calculate hkl corresponding to the peaks (at 2θ)

(I will share the excel file separately)

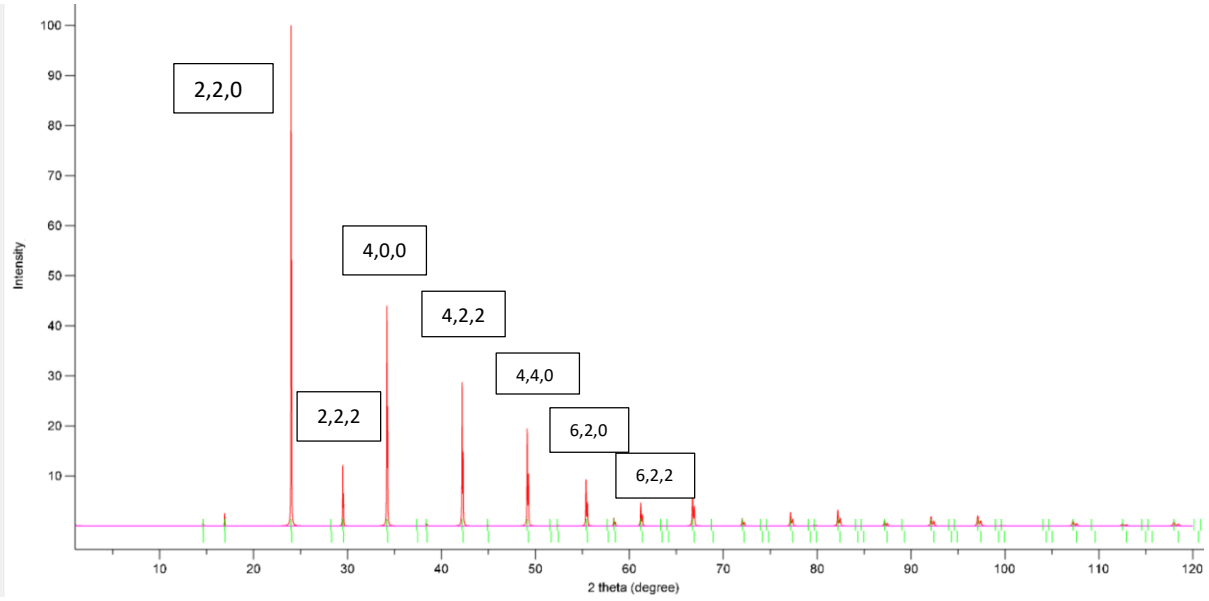

Figure 4: XRD with peaks labelled.(upto 60 degrees)

b) Comparison with Experimental Data

Since we used the CIF file for $Cs_2AgInCl_6$, we compare it with that of the experimental data with x = 1. (No substitution)

Data was normalized in the following way:

- Keep the minimum value as zero
- Divide all values by the maximum intensity. This results in the maximum intensity becoming 1.

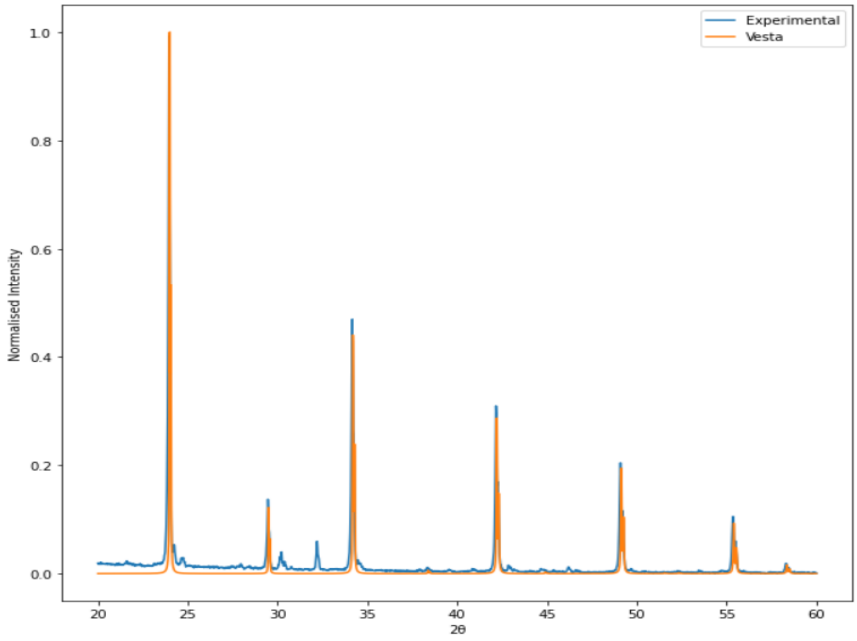

Figure 5: Comparison of experimental and Vesta simulated XRD patterns.

We find that the peaks are sufficiently close. Let us compute the 'a' value from the experimental data and check how close it is to the actual 'a'.

- Recognise that the first peak has maximum intensity. So let's choose it to calculate 'a'.
- We know that the peak corresponds to (220) plane.
- Use Bragg's law to obtain d. $d = \frac{\lambda}{2\sin\theta}$
- Now use $\frac{a^2}{d_{hkl}^2} = h^2 + k^2 + l^2$ to get 'a'.

Using the above method, $\mathbf{a_{Expt}}$ was found to be: **10.4964 Å** which is very close to the Vesta value of 10.4806 Å. Note that since the structure is cubic, we have a=b=c.

c) a vs x plot

The above process to calculate 'a' was repeated utilizing the experimental data for different composition ('x'). The results are tabulated below:

X	0	0.2	0.4	0.6	0.8	1
a (in Å)	10.771	10.735	10.654	10.610	10.548	10.496

Note that since the structure is cubic, we have a=b=c.

The above data was used to plot a vs x.

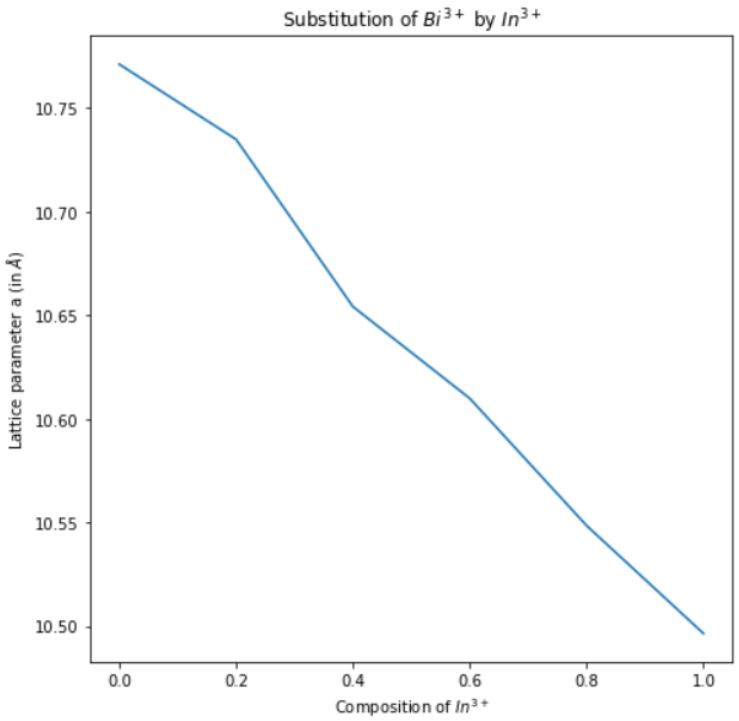

Figure 6: a vs x plot for substitution of In^{3+} by Bi^{3+}

As we have seen in class, we again see a linear variation, this is expected.

Ionic radii from Shannon's book:

BI+3 6S 2	V	1.10	.96	C
	VI	1.17	1.03	R*
	VIII	1.31	1.17	R
IN+3 4D10	IV	.76	.62	
	VI	.940	.800	R*
	VIII	1.06	.92	RC

We have a coordination number of 6 in this structure (for both In^{3+} and Bi^{3+})

Ionic Radius of In^{3+} = 0.92 Å

Ionic Radius of Bi^{3+} = 1.03 Å

Since Bi^{3+} is larger, if we substitute more of In^{3+} with Bi^{3+}, the crystal size keeps getting larger!

This explains the linear increase in the graph. (**more substitution => larger the crystal size**)

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(5)

a) $\phi \rightleftharpoons Bi_{In}^{x}$

Bi^{3+} and In^{3+} are in same oxidation state so no charge (excess or deficiency) has been introduced

$\Rightarrow$ No conductivity introduced

b) $\phi \rightleftharpoons \ddot{Bi}_i + 3e'$

Excess electrons introduced $\Rightarrow$ n-type conductivity

c) $\phi \rightleftharpoons V_{Cl}^{\bullet} + e'$

Excess e's introduced $\Rightarrow$ n-type conductivity

d) $\phi \rightleftharpoons V_{Ag}' + h^{\bullet}$

Excess holes introduced $\Rightarrow$ p-type conductivity.

e) $\phi \rightleftharpoons Mg_{In}' + h^{\bullet}$

Excess holes introduced $\Rightarrow$ p-type conductivity