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CH18B020

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

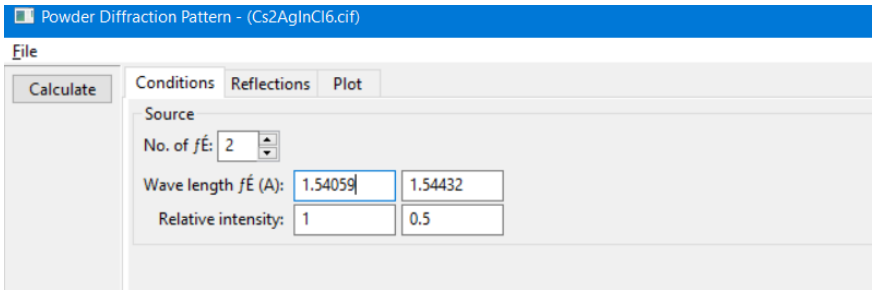

Figure 2: Applying the appropriate wavelengths in Vesta

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

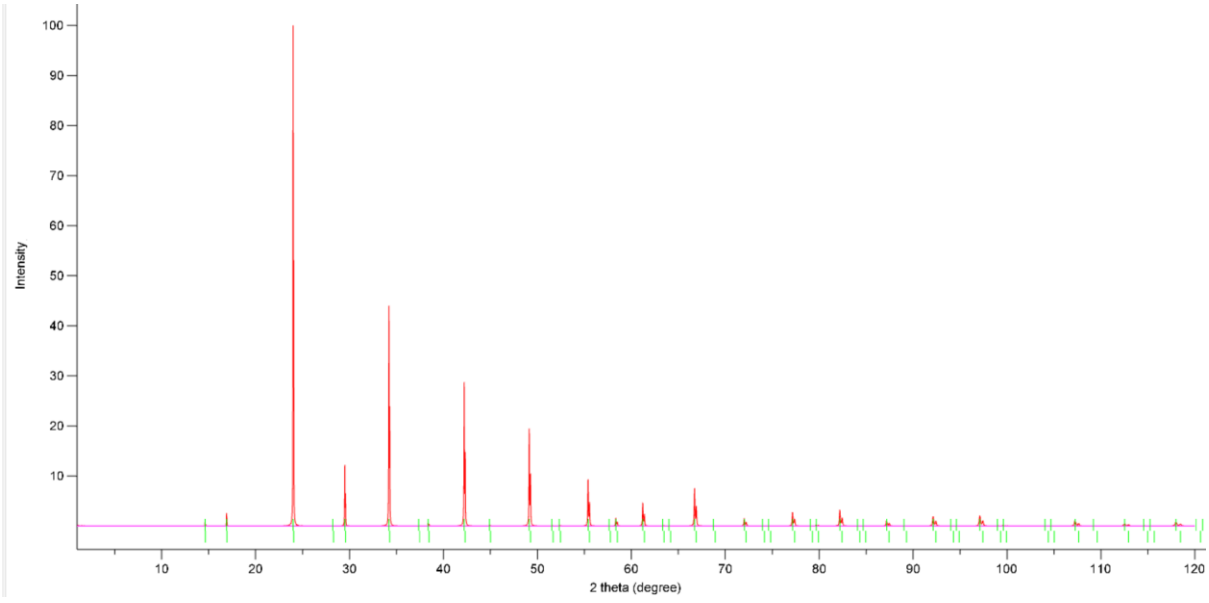

Figure 3: XRD Pattern of $Cs_2AgInCl_6$

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)

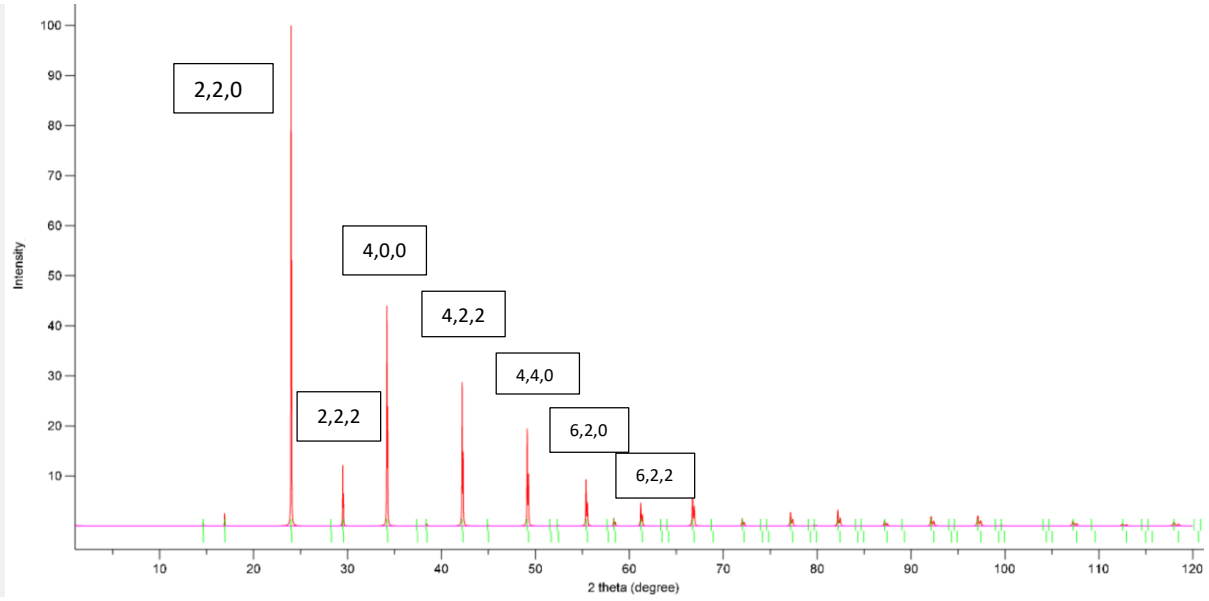

Figure 4: XRD with peaks labelled.(upto 60 degrees)

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.

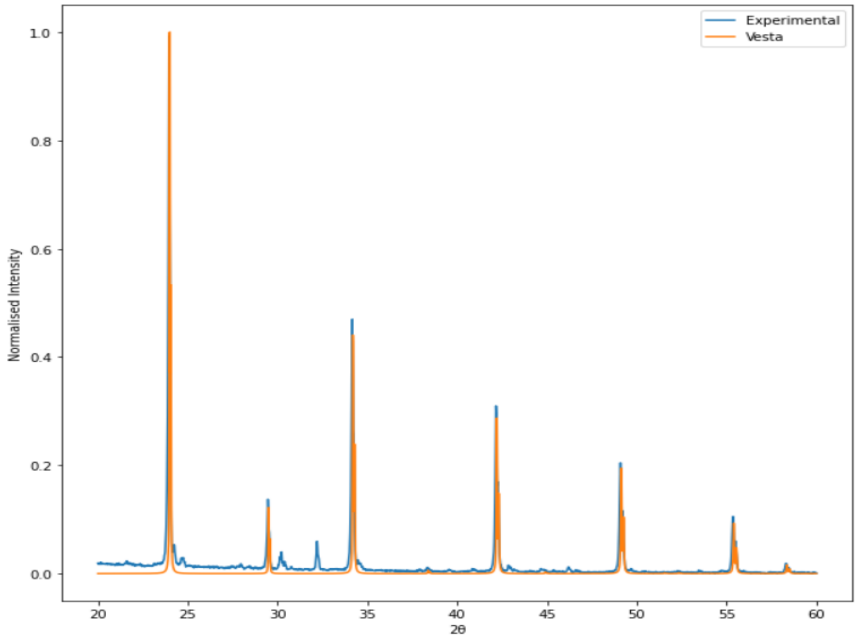

Figure 5: Comparison of experimental and Vesta simulated XRD patterns.

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.

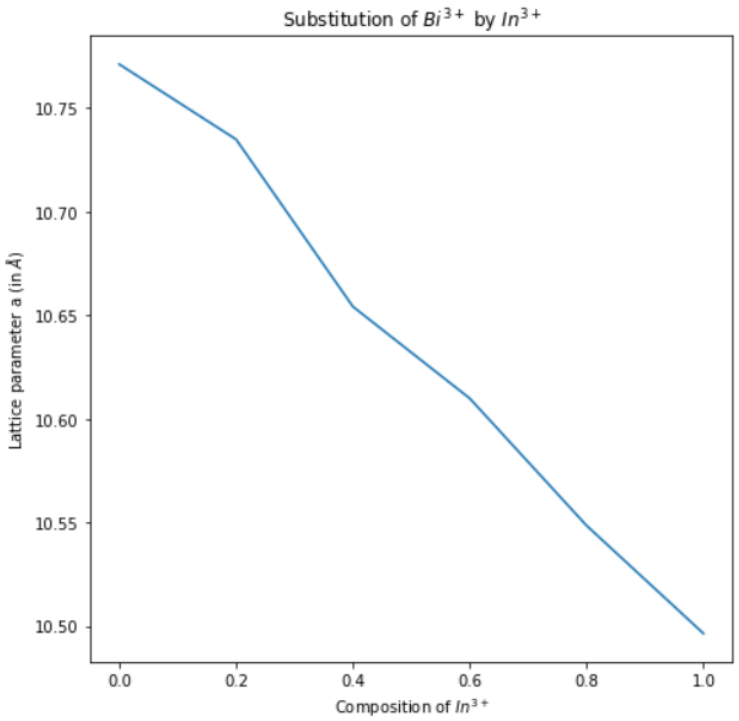

Figure 6: a vs x plot for substitution of In^{3+} by Bi^{3+}

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**)