पदार्थविज्ञानम्

MATERIALS SCIENCE

22-03-2023

Bonding

Primary
- Covalent
  - directional
  - high strength
  - low electrical conductivity (increased by doping)
  - low thermal conductivity
- Ionic
  - strong bond
  - electrical/thermal conductivity
    - (low or moderate)
- Metallic

Secondary
- van der Waals bond

van der Waals bond :

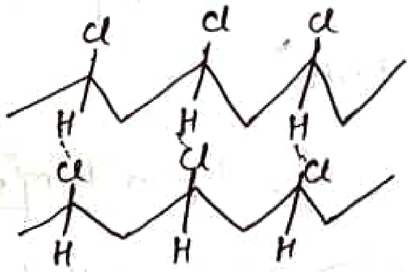
① London force: instantaneous dipole moment – inst. dipole moment (CCl_4 ···)

② Debye force: permanent d.m. – induced d.m. (HCl --- Ar)

③ Keesom force : permanent d.m. – permanent d.m. ($H_2O \cdots H_2O$)
(e.g., hydrogen bond)

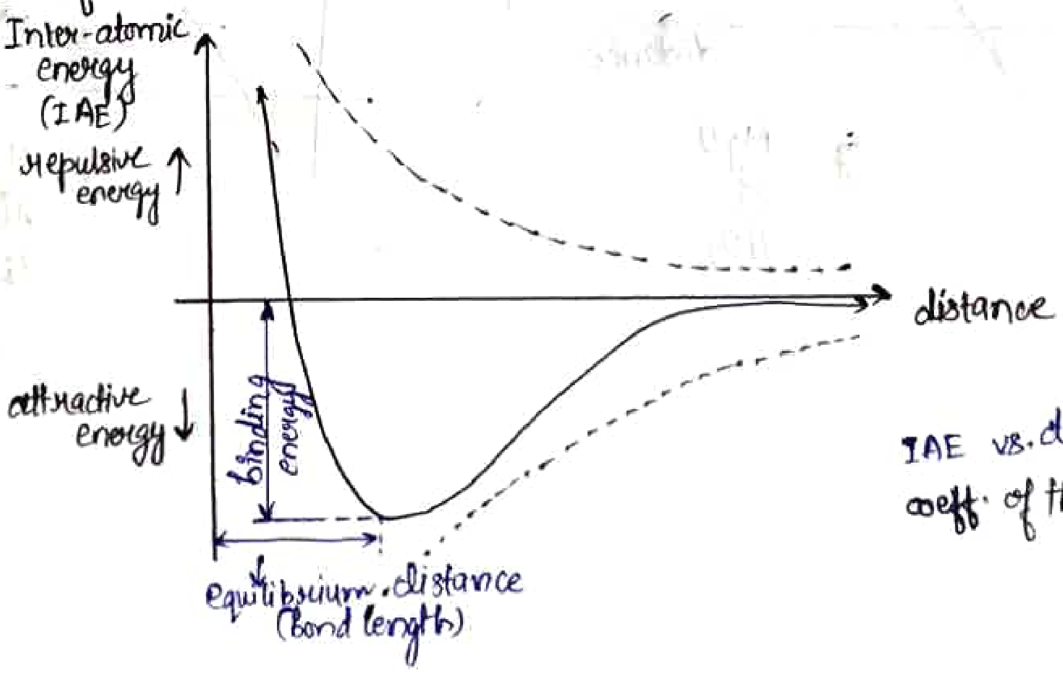
PVC:

$-(CH_2-CHCl)_n-$



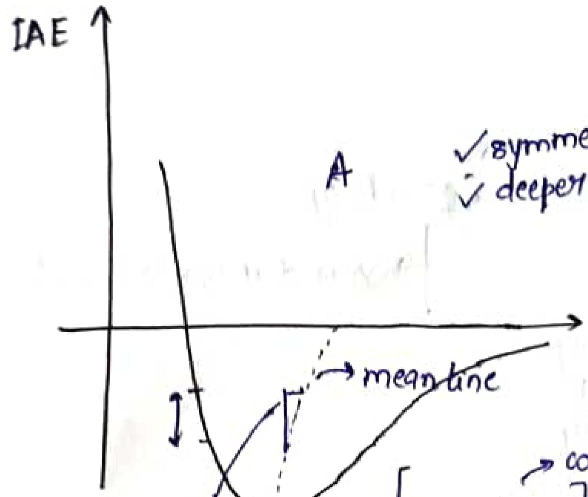
→ brittle
additives (pthalate)
breaks H-bond
(layers slide)
↓
flexible

Bond formation:



IAE vs. distance

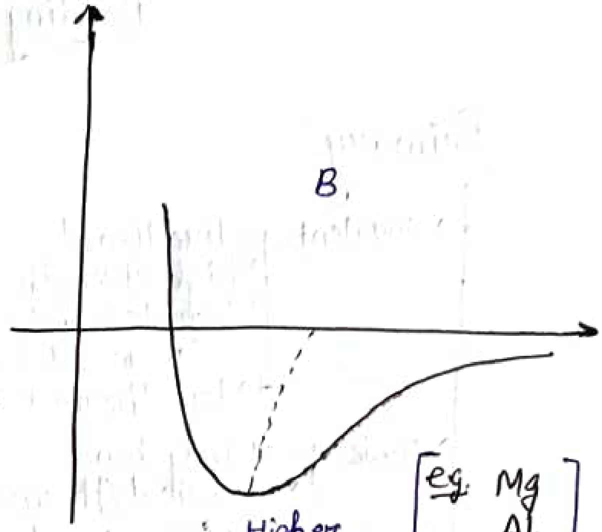
coeff. of thermal expansion $\propto \frac{dL}{dT}$



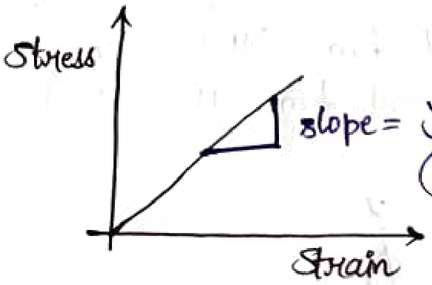
✓ symmetric
✓ deeper

variation in inter-atomic distance → low

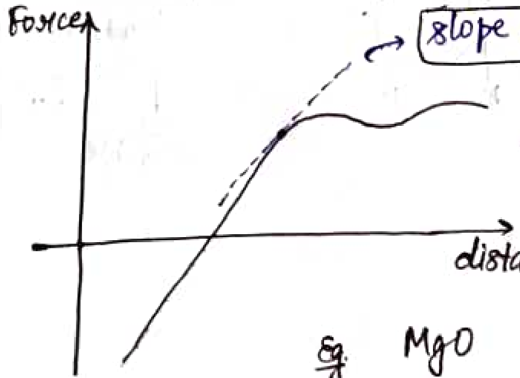
eg. [MgO → covalent bond, Al_2O_3, SiN, Si, Be]



Higher coeff. of thermal expansion ⟸ eg. [Mg, Al, Fe, Al, Mg]



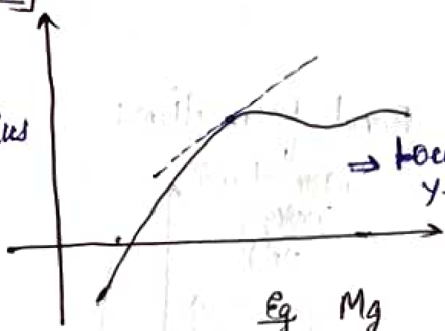
slope = Young's Modulus (Modulus of Elasticity)



$\boxed{\text{slope} \propto \text{Young's Modulus}}$

⇒ Higher Young's Modulus

eg. MgO
Si
TiO_2



⇒ Lower Y.M.

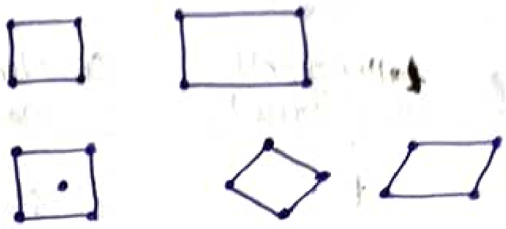
eg. Mg
Al
Ti

Atomic / Ionic Arrangement in Materials

Types of Arrangement (periodic)

1D 1 

2D 5



3D 14 - Bravais Lattice
↳ 7 crystal systems

Lattice structure = (Lattice (points)) + motif (basis)
↳ atoms / group of atoms periodically arranged on lattice.

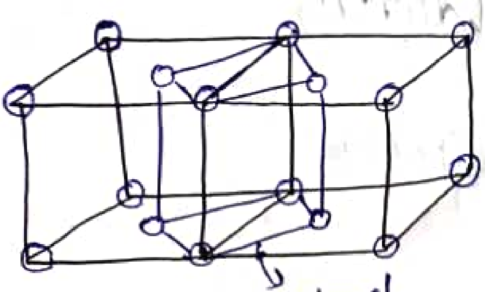
29-03-2023

→ 7 crystal systems ⇝ 14 crystal structures

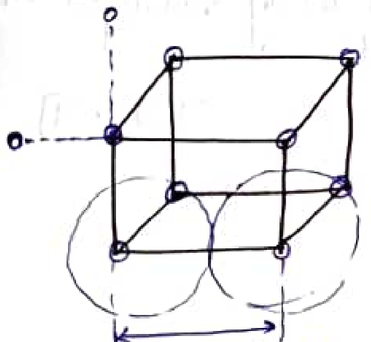
1. Cubic ⟶ Primitive (P), BCC, FCC
2. Tetragonal ⟶ P, BC
3. Hexagonal ⟶ P
4. Orthorhombic → P, BC, Base centric, FC
5. Rhombohedral → P
6. Monoclinic ⟶ P, base centric
7. Triclinic ⟶ P

Base centred cubic → ✗

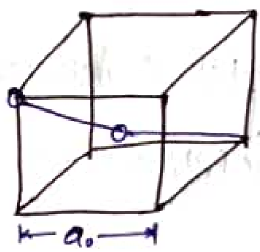
#



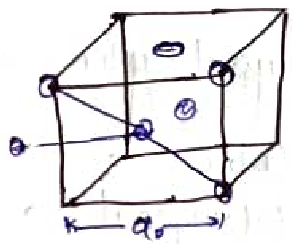
Crystal	Lattice points (No. of atoms)	Coordination no.	Unit cell parameter	Packing factor
SC	1	6	$a_0 = 2r$	0.52
BCC	2	8	$a_0 = \frac{4r}{\sqrt{3}}$	0.68
FCC (ccp) ↳ (abc, abc)	4	12	$a_0 = 2\sqrt{2}r$	0.74 → highest in cubic system
Hexagonal ↳ (ab, ab arrangement)	2	12	$a_0 = 2r$, $c = 1.63a_0$	0.74



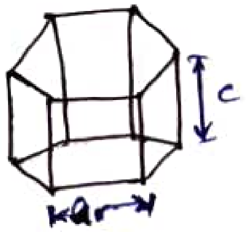
SC (Simple cube)



BCC (Body-centred cube)

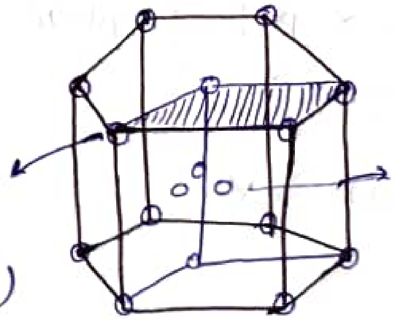


FCC (Face-centred cube)



hcp

$4\left(\frac{1}{3} \times \frac{1}{2}\right) + 4\left(\frac{1}{6} \times \frac{1}{2}\right) = 1 + 1$



Unit cell of hexagon (parallelopiped)

→ Density $(\rho) = \dfrac{\text{No. of atom} \times \text{atomic weight}}{\text{volume of unit cell} \times N_A}$

→ Packing factor $= \dfrac{\text{No. of atom} \times \text{Volume of atom}}{\text{volume of unit cell}}$ $(a)^3$

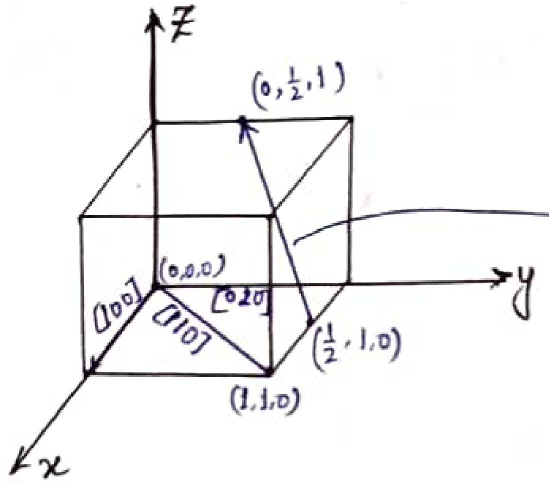
→ volume of hcp $= a^2 c \sin 60^\circ$

MILLER INDICES

Miller Indices Direction

↳ To represent direction

| # Axes → our choice



$\rightarrow (\frac{1}{2}, -\frac{1}{2}, 1) \rightarrow -1,-1,2$

↓

$[\bar{1}\,\bar{1}\,2]$

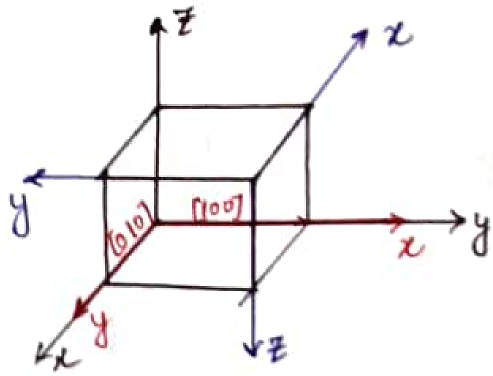
↳ # (no comma)

① Identify the coordinates.

② Subtract (head − tail).

③ Clear the fraction and deduce the least integer

④ Represent using [ ] (without comma).



[100] and [200] represent the same direction.

⇒ Family of directions

100
010
001
$\bar{1}$00
0$\bar{1}$0

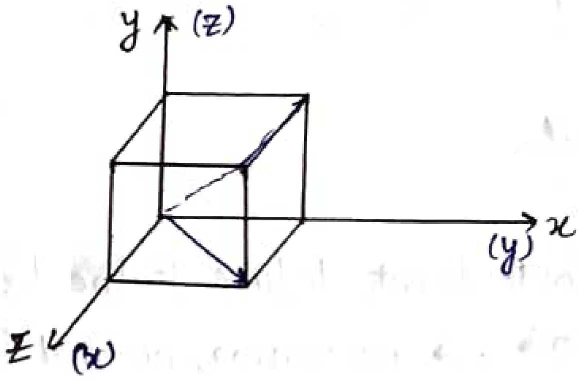
→ same family

⟨100⟩

8-04-2023

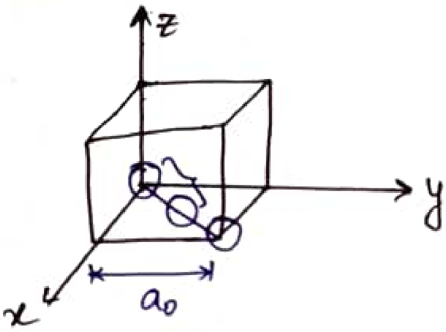
Miller Indices

↳ [h k l]



$\left.\begin{matrix}[1\ 1\ 0] \\ [0\ 1\ 1]\end{matrix}\right\}$ family

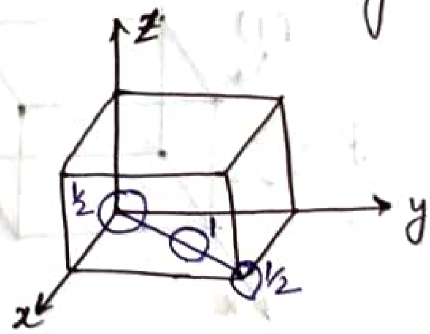
① **Repeat distance:** Distance b/w adjacent lattice point in a given direction.



FCC $[110] = \frac{a_0}{\sqrt{2}}$

$\frac{\sqrt{2}a_0}{2}$

② **Linear Density:** $= \frac{\text{no. of atom}}{\text{magnitude of dir}^n}$



FCC $[110] = \frac{a_0}{\sqrt{2}}$

FCC $[110] = \frac{2}{\sqrt{2}\,a_0} = \frac{\sqrt{2}}{a_0}$

↓

closed packed dir^n

SC → cpd → [100]

BCC → cpd → [111]

③ **Linear Packing Fraction:** $= \frac{\text{length occupied by atom}}{\text{magnitude of dir}^n}$

FCC $[110] = \frac{4r}{\sqrt{2}a_0} = 1$ $\quad [\because \sqrt{2}a_0 = 4r]$

FCC $[100] = \frac{2r}{\frac{4r}{\sqrt{2}}} = \frac{1}{\sqrt{2}}$

Miller Indices (Planes)

① Identify the intercepts.

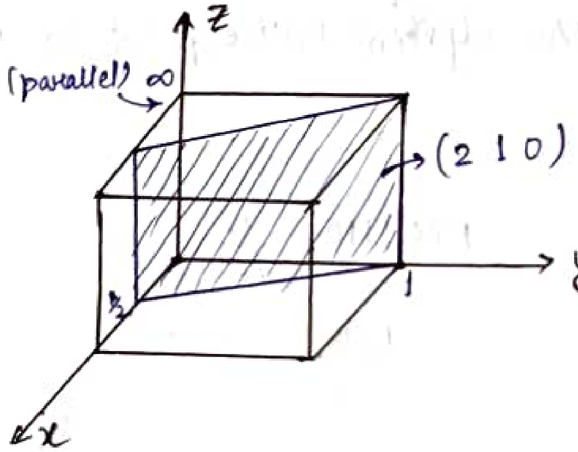
$\frac{1}{2}, 1, \infty$

② Take the reciprocal.

$2, 1, 0$

③ Remove fraction, but donot deduce to the lowest fraction.

$(2\ 1\ 0)$ ⇝ no comma, normal bracket.



→ If the plane passes through origin, shift the plane by 1 unit in -ve y-direction (or in +ve y-dirn).

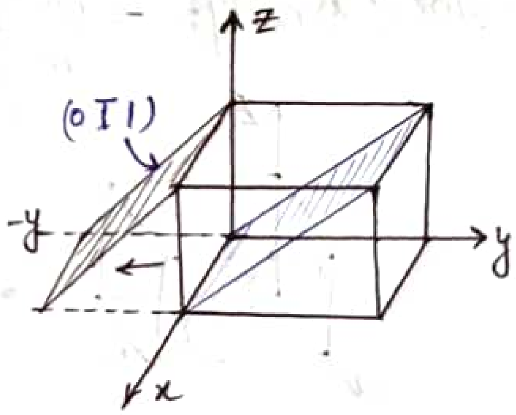
$\infty, -1, 1$

↓

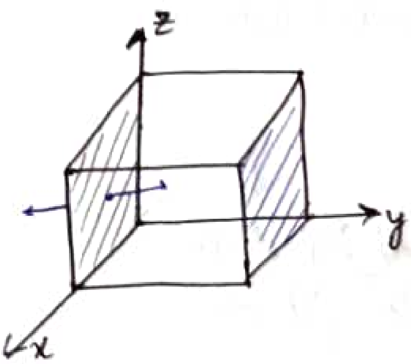
$0, -1, 1$

↓

$(0\ \bar{1}\ 1)$



Eg.



⇒

$\infty, 0, \infty$

↓

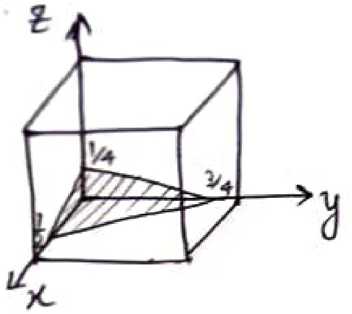
$0, \infty, 0$ → ✗

$\infty, 1, \infty$

$0, 1, 0$

$(0\ 1\ 0)$

Eg.



$\Rightarrow$

$$\frac{1}{2}, \frac{3}{4}, \frac{1}{4}$$
$$\downarrow$$
$$2, \frac{4}{3}, 4$$
$$\downarrow$$
$$(6, 4, 12)$$

Eg.

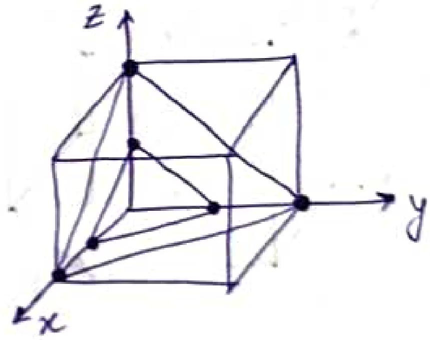
$(2, 2, 2) \rightarrow ?$

$\Downarrow$ take reciprocal

$\left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\right)$

x y z - intercepts

$\Rightarrow$



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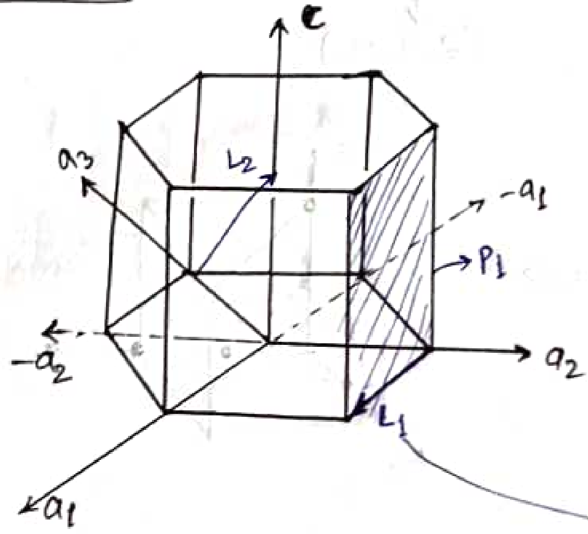
Hexagon

Lines (vectors):



$[h'\ k'\ l']$

direction $[h\ k\ i\ l]$

$h = \frac{1}{3}(2h' - k')$

$k = \frac{1}{3}(2k' - h')$

$i = -\frac{1}{3}(k' + h')$ $\boxed{h + k = -i}$

$l = l'$

head − tail

$(a_1, a_2, c) - (a_1, a_2, c)$

Eg. L_1: $(1, 1, 0) - (0, 1, 0)$

$[1\ 0\ 0] \rightarrow [h'\ k'\ l']$

$h = \frac{2}{3}, k = -\frac{1}{3}, i = -\frac{1}{3}, l = 0$

$\frac{2}{3}, \frac{-1}{3}, \frac{-1}{3}, 0$

$\downarrow$

$-2, -1, -1, 0$

$[h\ k\ i\ l] \equiv [2\ \bar{1}\ \bar{1}\ 0]$

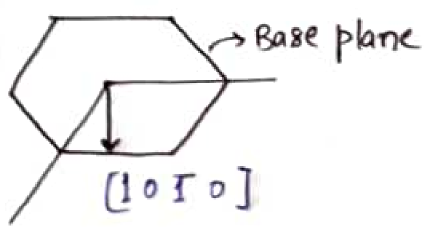
Eg. head − tail

L_2: $(0\ 0\ 1) - (-1, -1, 0)$

$(1\ 1\ 1) \rightarrow [h'\ k'\ l']$

$[h\ k\ i\ l] \rightarrow [1\ 1\ \bar{2}\ 3]$

Eg.



Planes : (h k i l)

h' k' l'

$\boxed{h+k=-i}$

Eg. P_1 :

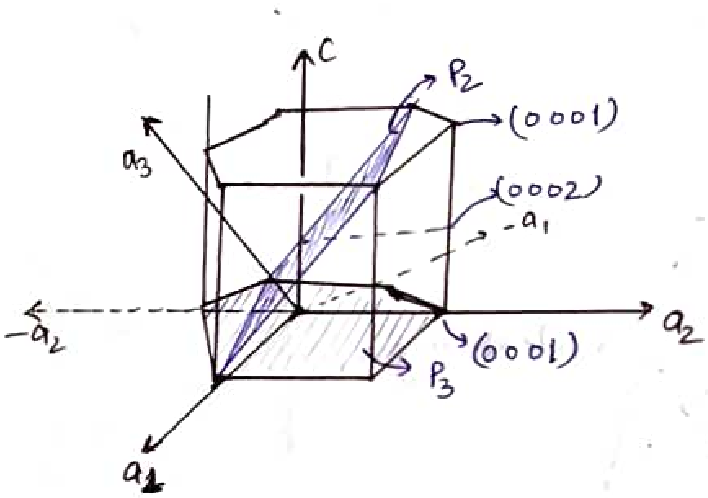
	a_1	a_2	c	
	∞	1	∞	→ intercept
	0	1	0	→ reciprocal

(0 1 0) → (h' k' l')

$(0\ 1\ \bar{1}\ 0)$ → (h k i l)

↳ $\boxed{h+k=-i}$

Eg.



P_2 :

a_1	a_2	c
1	$-\frac{1}{2}$	$\frac{1}{2}$
1	-2	2
1	-2	1 2

$(1\ \bar{2}\ 1\ 2)$

P_3 :

a_1	a_2	c	
∞	∞	1	← intercepts
0	0	1	

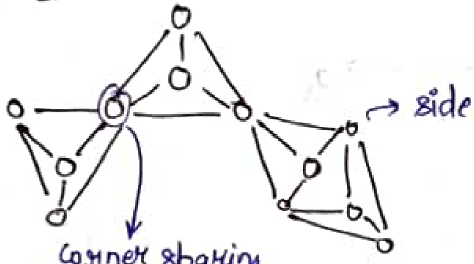
(0001) → (h k i l)

17-04-2023

Interstitial Sites (Voids)

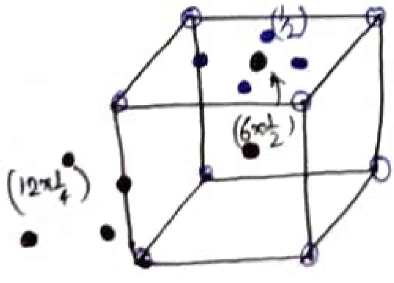
Voids	Coordination no.	Radius ratio
Linear	2	0 – 0.155
Trigonal	3	0.155 – 0.225
Tetragonal	4	0.225 – 0.414
Octahedral	6	0.414 – 0.732
Cubic	8	0.732 – 1

① Radius ratio
② Electrical neutrality
③ Polyhedra
eg, SiO_2

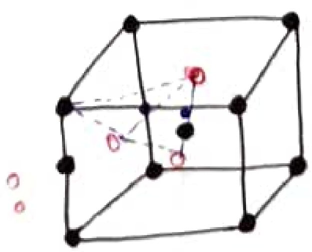


→

Crystal	Tetrahedral voids (TV)	Octahedral voids (OV)
BCC	$24\times\frac{1}{2}=12$	$6\times\frac{1}{2}+12\times\frac{1}{4}=6$
FCC	8	$1+12\times\frac{1}{4}=4$
hcp	$2+3+3+\left(\frac{1}{3}\times2\times6\right)=12$	6



Bcc



FCC

• → OV
• → TV

Common Crystal Structures

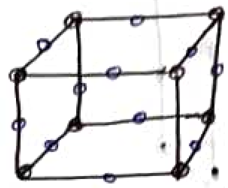
① NaCl (Rock Salt)

$Na^+ = 0.97 \mathring{A}$

$Cl^- = 1.81 \mathring{A}$

→ FCC

→ $\frac{Na^+}{Cl^-} = 0.53$ → OV

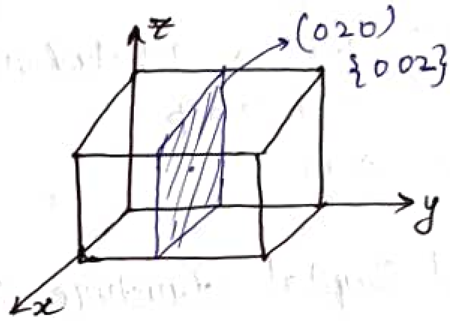


② CsCl (BCC Type)

$Cs^+ = 1.67 \mathring{A}$

$Cl^- = 1.81 \mathring{A}$

→ $\frac{1.67}{1.81} = 0.92$



③ Zinc Blende (ZnS)

$Zn^{2+} = 0.74 \mathring{A}$

$S^{2-} = 1.81 \mathring{A}$

Coordination of Zn^{2+}:

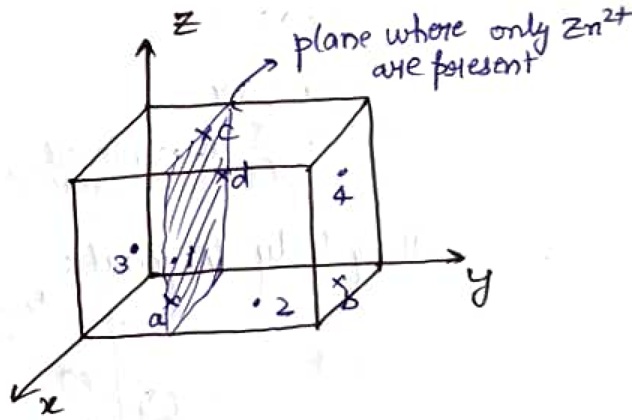
ZnS_4

① $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ⓐ $\frac{3}{4}, \frac{1}{4}, \frac{1}{4}$

② $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$ ⓑ $\frac{1}{4}, \frac{3}{4}, \frac{1}{4}$

③ $\frac{3}{4}, \frac{1}{4}, \frac{3}{4}$ ⓒ $\frac{1}{4}, \frac{1}{4}, \frac{3}{4}$

④ $\frac{1}{4}, \frac{3}{4}, \frac{3}{4}$ ⓓ $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$



18-04-2023

④ Fluorite Structure (CaF_2), ZrO_2, UO_2, CeO_2

$Ca^{2+} = 0.99$

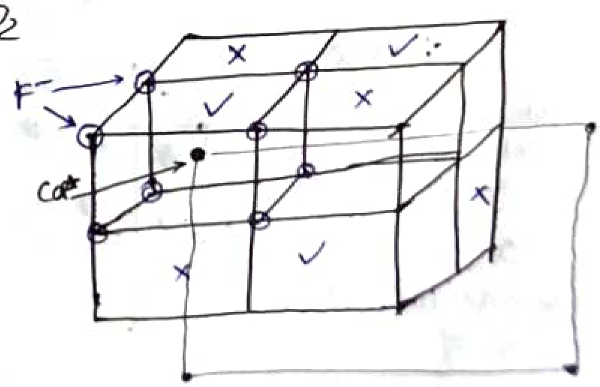
$F^- = 1.33$

Ratio = 0.744

→ Ca_4F_8

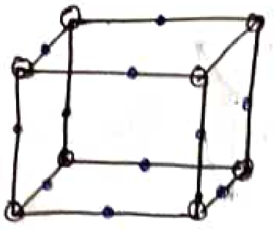
Another way to visualise: Ca^{2+} → FCC

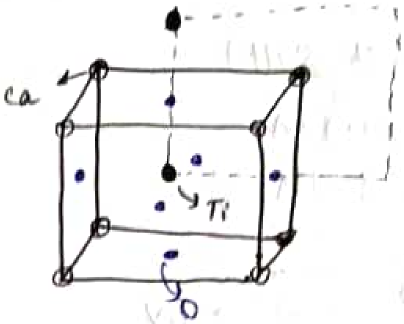
F → tetrahedral position



⑤ Perovskite ABX_3 ($CaTiO_3$)

PZT → SC, BC, FC





⑥ Corundum (Al_2O_3)

$Al^{3+} = 0.57$ ⇝ octahedral voids (4 out of 6 occupied)
↳ 2 up, 2 down
2 free ⇝ 1 up, 1 down

$O^{2-} = 1.31$ ⇝ hcp

Ratio = 0.43

⑦ Diamond Crystal Structure (DC Type) → Diamond cubic

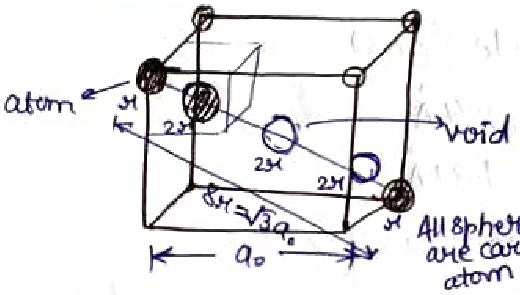
e.g., Sn, Si

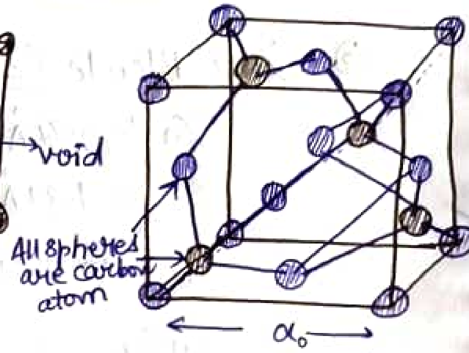
• All carbons are tetrahedrally covalent bonded.

C → FCC

$\sqrt{3}\,a_0 = 8r$

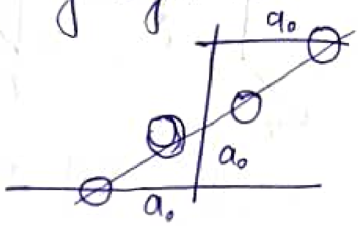
$\Rightarrow \boxed{a_0 = \frac{8}{\sqrt{3}} r}$ → Unit cell parameter





DC unit cell

Along body diagonal:



$\sqrt{3}\,a_0 = 8r$

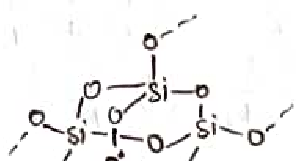
• No. of C-atoms in unit cell = 8

• Diamond (carbon), Si, Ge, Sn, etc. has DC structure.

⑧ SiO_2 ⇝ β-cristobalite form

26-04-2023

$\frac{Si^{4+}}{O^{2-}} = \frac{0.42}{1.31} = 0.318$ ↳ Tetrahedral voids



Si → FCC

Alternate tetrahedral (of big)

Si = 8

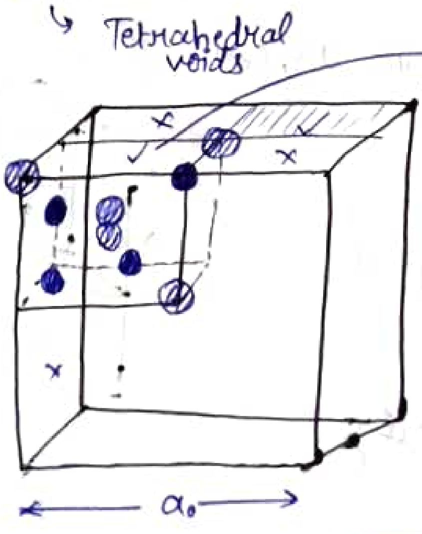
O = 16

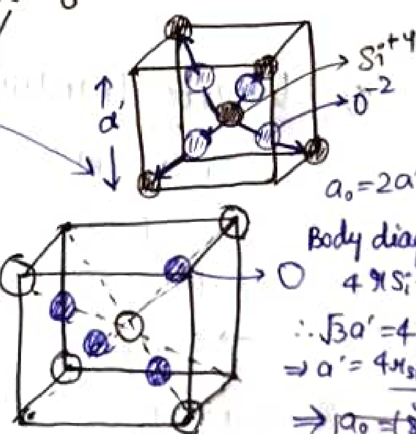
In one unit cell,

no. of $Si^{4+} = 8$

no. of $O^{2-} = 16$

● → O





Body diagonal $= 4r_{Si} + 4r_O$

$\therefore \sqrt{3}\,a' = 4r_{Si} + 4r_O$

$\Rightarrow a' = \frac{4r_{Si} + 4r_O}{\sqrt{3}}$

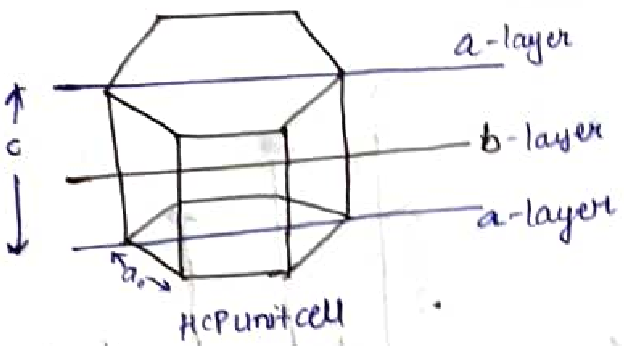
$\Rightarrow \boxed{a_0 = (8r_{Si} + 8r_O)/\sqrt{3}}$

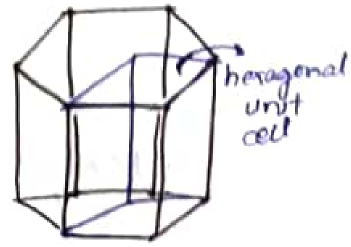
chemical formula of one unit cell: Si_8O_{16}

Compositional formula = SiO_2

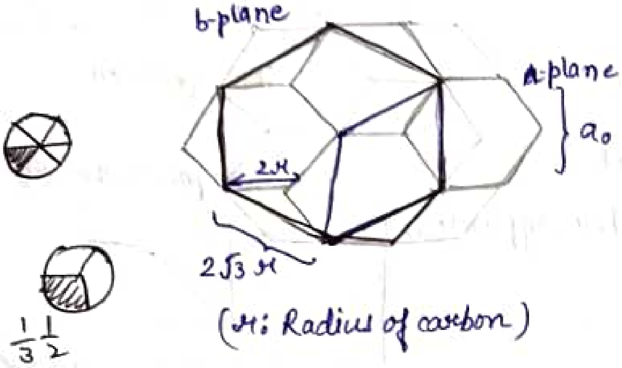
2-05-2023

⑧ Graphite (hcp)



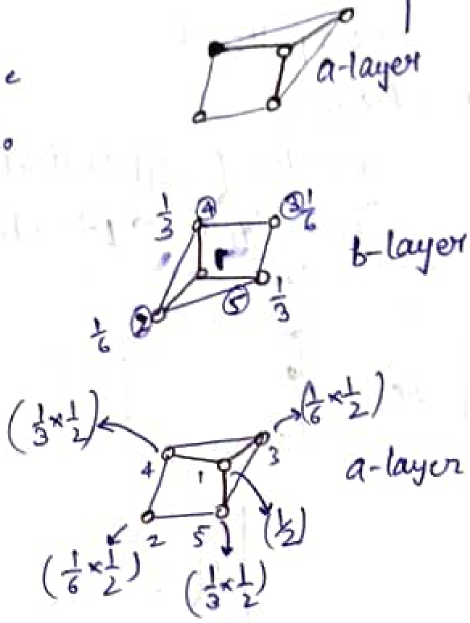


C=4



(r: Radius of carbon)

$\boxed{a_0 = 2r\sqrt{3}}$



Total no. of carbon atom in the unit cell (parallelopiped) = 4.

⑨ Spinels : $\overset{2+}{A}\overset{3+}{B_2}\overset{2-}{O_4}$

eg, $MgAl_2O_4$ (spinel), Mn_3O_4, $ZnFe_2O_4$, $FeCr_2O_4$.

$\downarrow$

$Mg_8Al_{16}O_{32}$

8 FCC, oxygen

tetrahedral – 64 , 8 → Mg ⇝ ($\frac{1}{8}$th of tetrahedral voids)

octahedral – 32 , 16 → Al ⇝ ($\frac{1}{2}$ of octahedral voids)

⑩ Inverse Spinel ($B(AB)O_4$):

e.g., $NiFeO_4$

Ni → A, Fe → B

8 tetrahedral – B^{3+} ⇝ ($\frac{1}{2}$) ⇝ ($\frac{1}{8}$th of T.V.)

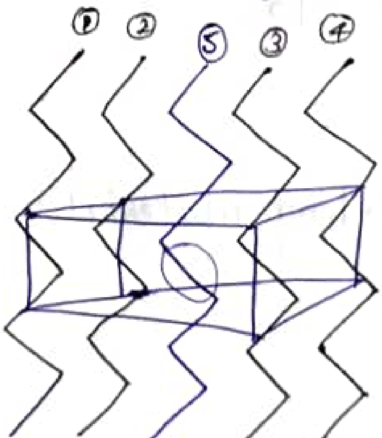
8 octahedral – B^{3+} ⇝ ($\frac{1}{2}$) → ($\frac{1}{4}$th of O.V.)

8 octahedral – A^{2+} ⇝ ($\frac{1}{4}$th of O.V.)

Polyethylene

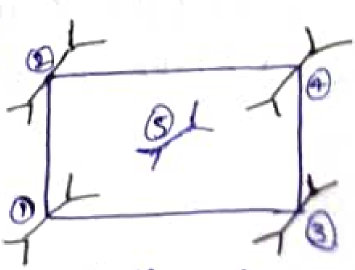
$+CH_2-CH_2+_n$

~~source~~



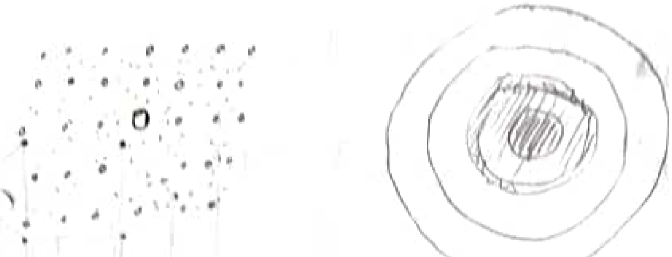
Orthorhombic unit cell

C_4H_8



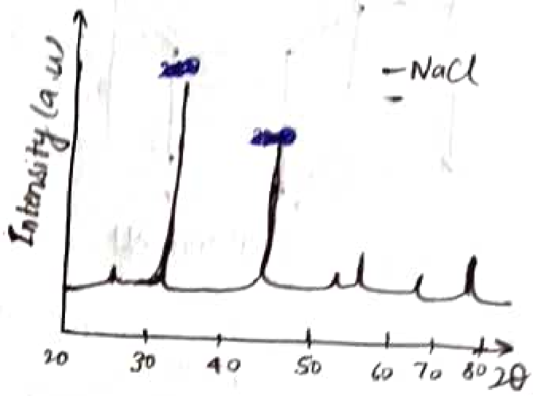
In one unit cell, 4-C
8-H

X-RAY DIFFRACTION (XRD)



Single crystalline   poly crystalline

XRD patterns

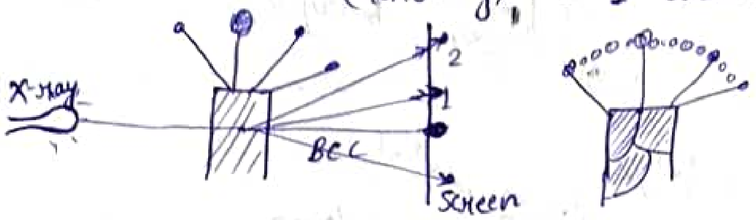


XRD spectrum

$\boxed{n\lambda = 2d\sin\theta}$

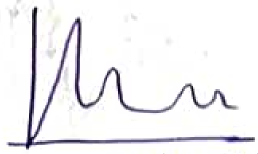
n: order of diffraction

(Generally, n = 1 → 1st order diffraction)



For amorphous, no diffraction

For amor. + crystalline.



polycrystalline

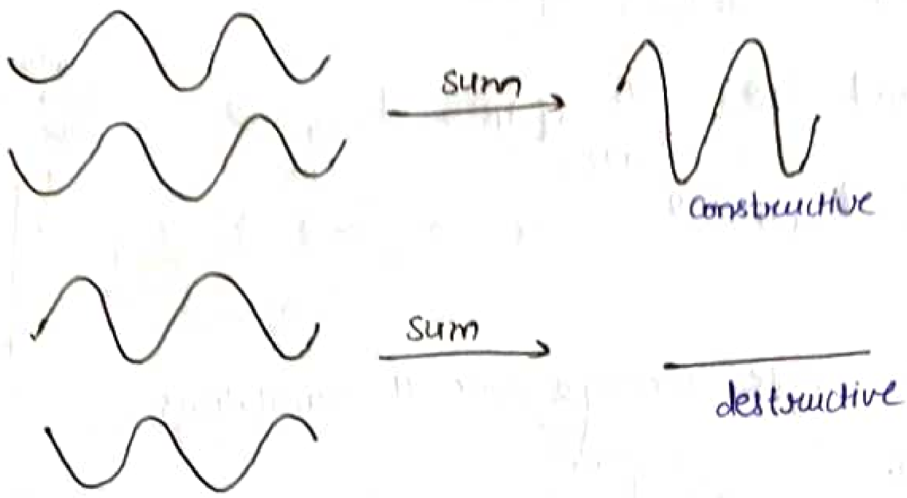
~~# (SC(100)~~
~~BCC(110)~~

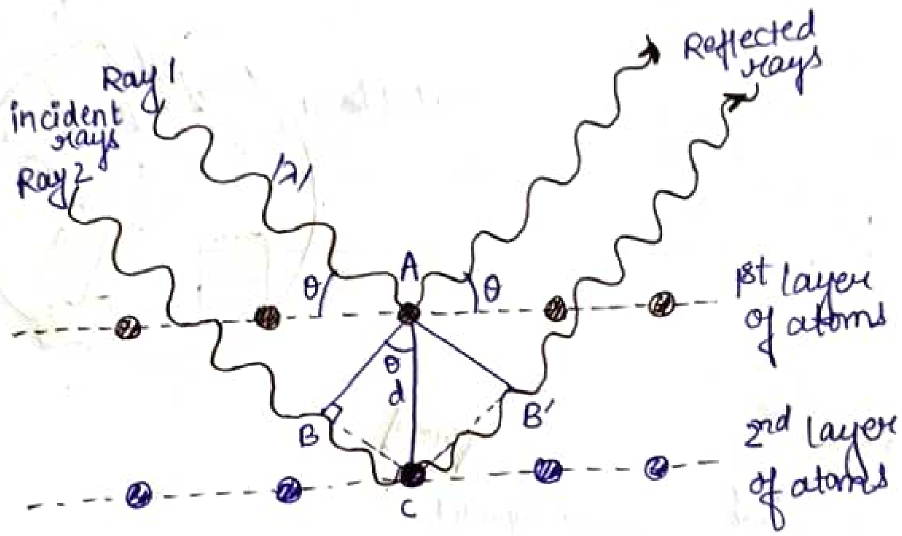
Discovery of X-rays

↳ X-rays are electromagnetic radiation with wavelength $\sim 1\text{Å} = 10^{-10}$ m (visible light $\sim 5.5\times10^{-7}$ m).

- Wilhelm Conrad Röntgen 1895.
- Nobel Prize in 1901.
- Particle or wave?
- Make shadows of absorbing material on photosensitive paper.

→ Constructive and destructive interferences:





① compared to ray 1, ray 2 travels an extra distance

$BC + CB' = 2BC$

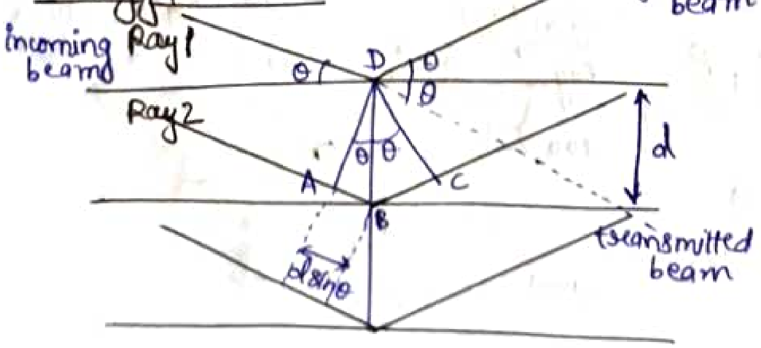
② This extra distance must equal a multiple of λ in order for the interference with with ray 1 to be constructive : $n\lambda = 2BC$.

③ Since AC is the hypotenuse of a right triangle ABC,

$BC = d\sin\theta$

④ so, $\boxed{n\lambda = 2BC = 2d\sin\theta}$.

Bragg's law



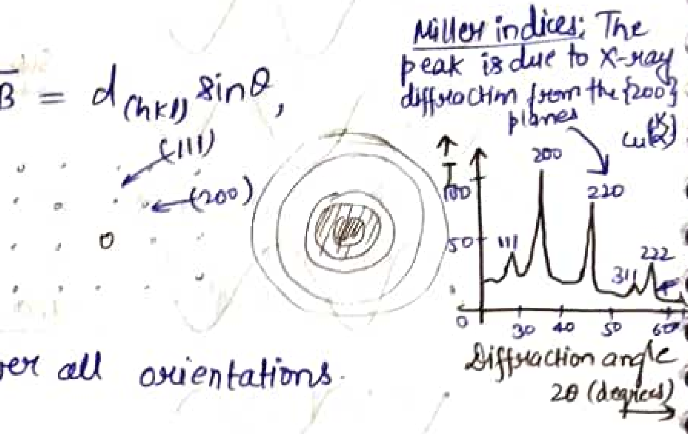
For constructive interference (diffraction) of the scattered x-rays, it is required that the beams, scattered on successive planes be "in phase" after they leave the surface of the crystal.

Constructive interference occurs only when

$$\overline{AB} + \overline{BC} = n\lambda \qquad (n = 1, 2, 3, \dots)$$

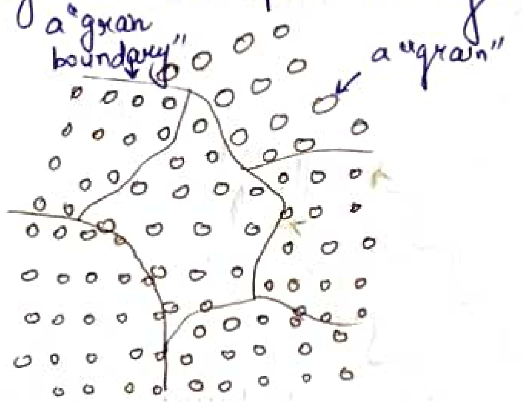
Since $\overline{AB} = \overline{BC}$ and $\sin\theta = \dfrac{\overline{AB}}{d_{(hkl)}} \Rightarrow \overline{AB} = d_{(hkl)} \sin\theta$,

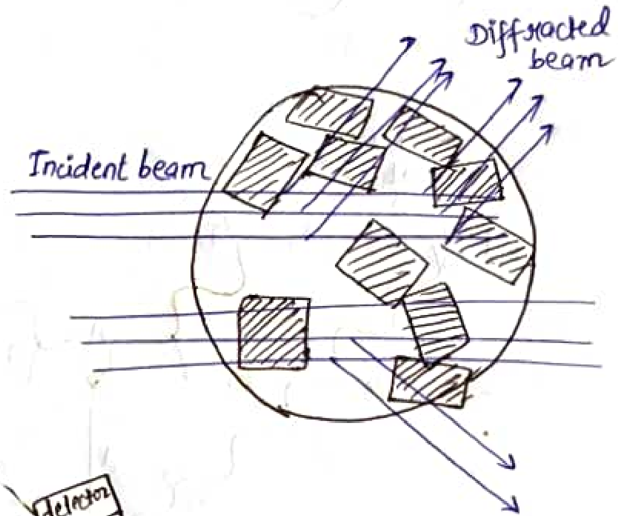
$$\therefore\ n\lambda = 2d_{(hkl)} \sin\theta$$

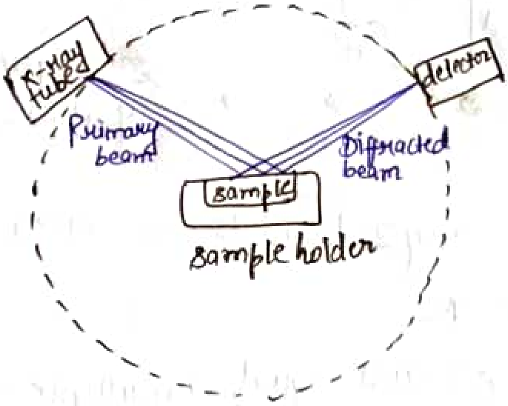


why rings?

↳ Polycrystalline sample average over all orientations.







Miller Indices

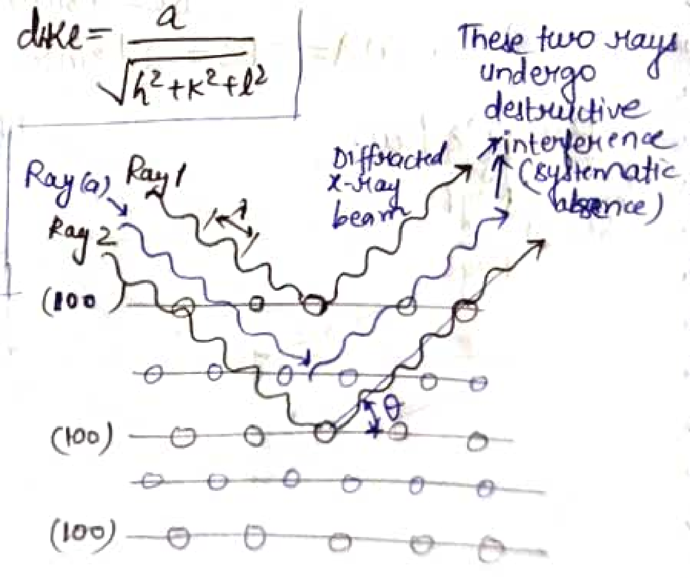
Cubic: $\dfrac{1}{d^2} = \dfrac{h^2+k^2+l^2}{a^2}$ – or – $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

Tetragonal: $\dfrac{1}{d^2} = \dfrac{h^2+k^2}{a^2} + \dfrac{l^2}{c^2}$

Hexagonal: $\dfrac{1}{d^2} = \dfrac{4}{3}\left(\dfrac{h^2+hk+k^2}{a^2}\right) + \dfrac{l^2}{c^2}$

Path difference b/w Ray 1 & 2 = λ

Path difference b/w Ray 1 & (a) = $\lambda/2$



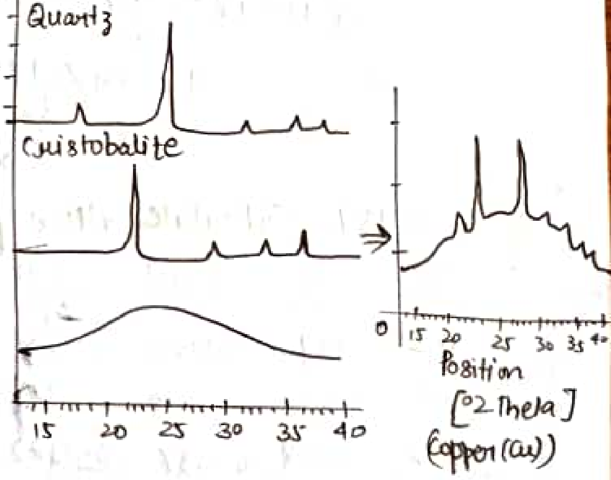
Systematic Absence

Consider cubic system. Cubic system has 3 types of arrangements: simple cube, center cube (BCC) and FCC (face center cube).
The simple cube have diffraction from all the planes. But BCC and FCC have diffractions only from some specific planes.
The differences arise b/c the centering (presence of body center or face center atom) leads to destructive interference for some reflections and the missing reflections are known as systematic absences.
The systematic absence can be concluded as:

simple cube (primitive): all (hkl) values show diffractions.
BCC: $h+k+l=$ even
FCC: h, k, l (either all odd or all even).

The above mentioned absence abridged in the table:

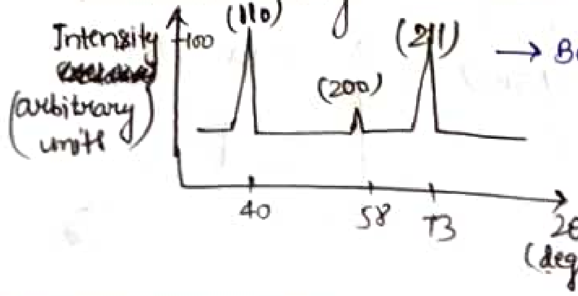
Primitive, P	Face centered, F	Body centered, B	Corresponding hkl	Forbidden no.s
1			100	
2		2	110	
3	3		111	
4	4	4	200	
5			210	
6			211	
				7
8	8	8	220	
9			221, 300	
10		10	310	
11	11		311	
12	12	12	222	
13			320	
14		14	321	
				15
16	16	16	400	



Crystal Structure and Calculation of Lattice Parameters

Lattice parameter 'a' from the indexed XRD spectrum.

Eg. The x-ray diffraction pattern of crystalline iron is given below. The crystal structure belongs to the cubic system. Calculate the lattice constant. Given $\lambda = 0.154$ nm.



→ BCC (Cu K_α - radiation)

Soln: $\lambda = 2d\sin\theta$

$\Rightarrow d = \frac{\lambda}{2\sin\theta} = 0.225\ nm$

lattice parameter $a = d \times \sqrt{h^2+k^2+l^2}$

$= 0.225\sqrt{2}$

$= 0.318\ nm$.

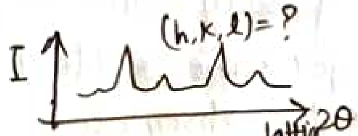
Take any indexed peak.

$(hkl) = (110)$

$2\theta = 40°$

$\theta = 20°$

$\Rightarrow \sin\theta = 0.342$

Eg. 

unit cell, lattice parameter ?

Multiply with a common factor to get whole no. (here it is 3). This is $(h^2+k^2+l^2)$.

2θ	θ	$\sin\theta$	$\sin^2\theta$	$\sin^2\theta/\sin^2\theta_{min}$	$\times 3$	Index(hkl)
38.52	19.26	0.3299	0.1088	1	3	(111)
44.76	22.38	0.3807	0.1450	1.333	4	(200)
65.14	32.57	0.5383	0.2898	2.664	8	(220)
78.26	39.13	0.6311	0.3983	3.661	11	(311)
82.47	41.235	0.6591	0.4345	3.994	12	

$h^2+k^2+l^2 = \frac{4a^2\sin^2\theta}{\lambda^2}$

all even/odd $\Rightarrow$ FCC

As $\lambda = 1.54\ nm$

$\Rightarrow a = 0.404\ nm$

Eg. $\lambda = 0.154$. Calculate lattice parameter & unit cell.

2θ	θ	$\sin\theta$	$\sin^2\theta$	$\sin^2\theta/\sin^2\theta_{min}$	$\times 2$	(hkl)
20.2	10.1	0.1753	0.0308	1	2	(110)
28.7	14.35	0.2478	0.0615	2	4	(200)
35.36	17.68	0.3037	0.0922	3	6	(211)
41.07	20.535	0.3508	0.01230	4	8	(220)
46.19	23.095	0.3922	0.1539	5	10	(310)
50.91	25.455	0.4298	0.1847	6	12	(222)
55.28	27.64	0.4639	0.2151	7	14	(321)

(no (hkl) for 7 so multiply by 2)

$\Rightarrow$ BCC

Eg. Fe BCC unit cell

radius of Fe = 0.126 nm, $\lambda = 0.154\ nm$

Draw the XRD spectrum of BCC Fe.

Soln: BCC: $\sqrt{3}a = 4r \Rightarrow a = 0.290\ nm$

$h+k+l$ = even

~~100~~

110

~~111~~

200

~~210~~

~~211~~

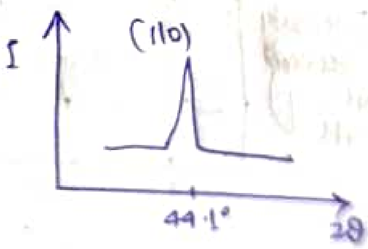
220

$\Rightarrow$ 110, 200, 211, 220.

$d = \frac{0.290}{\sqrt{1+1+0}} = 0.2057\ nm$

$\therefore 0.154 = 2 \times 0.2057 \sin\theta$

$\Rightarrow \sin\theta = 22.050°$

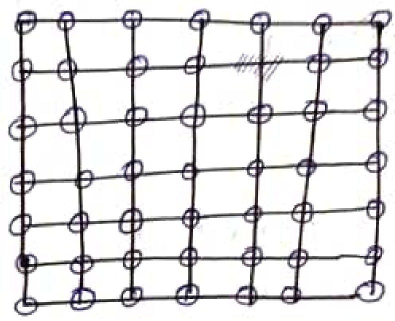


29-05-2023

IMPERFECTIONS IN CRYSTALLINE MATERIALS

- → ① Point defects
- → ② Line defects (Dislocation)
- → ③ Surface defects

Point Defects



ⓐ Vacancy defect ⇝ happens during processing

No. of vacancy,

$$n_v = n e^{-\frac{Q_v}{RT}},$$

n : atoms/cm^3

Q_v : energy required

$R = 8.314$

T : Temp. in kelvin.

Defect ↑ as Temp ↑

Q/ calculate the no. of vacancy in Cu(FCC) at 25°C. If we want to increase the no. of vacancy 1000 times, what should be the temp.?

($Q = 83680$ J/mol)

($a_0 = 0.3615$ nm)

Soln: Cu(FCC) → 25°C

$$n = \frac{4}{(3.615 \times 10^{-8} m)^3}$$

$$= 8.46 \times 10^{22} \text{ atoms/cm}^3$$

$$\therefore n_v = n e^{-\frac{Q_v}{RT}}$$

$$= 8.46 \times 10^{22} \times e^{-\frac{83680}{8.314 \times 298}}$$

$$= 1.8249 \times 10^{8} \text{ vacancies/cm}^3$$

OFHC copper ⇝ ultrapure copper with negligible defects

↳ space grade copper

↳ oxygen free, highly conducting.

Now,

$$n_v' = 1000\, n_v$$

$$\Rightarrow 1.8249 \times 10^{11} = 8.46 \times 10^{22} \times e^{-\frac{83680}{8.314 \times T}}$$

$$\Rightarrow T = 374.6 K$$

$$\approx 375 K$$

Q) BCC, Fe, $\rho = 7.874\ g/cm^3$
No. of vacancies / unit-cell ?

$$\left[\begin{array}{l} a_0 = 2.866 \times 10^{-8}\ cm \\ \text{At. wt. of Fe} = 55.847\ g/mol \end{array}\right]$$

Soln: $\rho = \dfrac{x \times at.wt.}{(a_0)^3 \times N_A}$ → density of defect-material

$$\Rightarrow x = \frac{7.874 \times (2.866 \times 10^{-8})^3 \times 6.022 \times 10^{23}}{55.847}$$

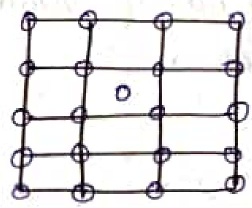
$$= 1.9987$$

$n = 2$

$\therefore$ Vacancy $= 2 - 1.9987$
$= 0.0013$/unit cell

$\Rightarrow$ 13 vacancies in 1000 unit cell.

(b) Interstitial defect ⇝ Interstitial position is occupied by some other atom (not the atom of the crystal).



↓
Eg. BCC Fe
C → at tetrahedral voids

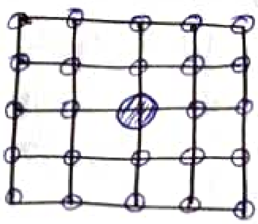
Theoretical Atomic % of C?

Soln: $\dfrac{\overset{\rightarrow \#C}{12}}{\underset{\swarrow \#C}{12} + \underset{\searrow \#Fe}{2}} = 86\%$

$$\left[\begin{array}{l} n_{TV} = 12 \\ 12C + 2Fe \end{array}\right]$$

Actual steel contains less than 12 % C.

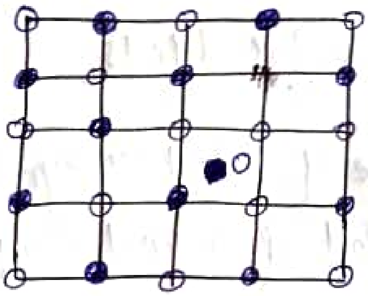
(c) Substitution defect
↳ slight distortation may be present.



Eg. Cu-Ni alloy : Ni replaces Cu.
NiO in MgO : MgO replaces NiO.

(d) Frankel defect

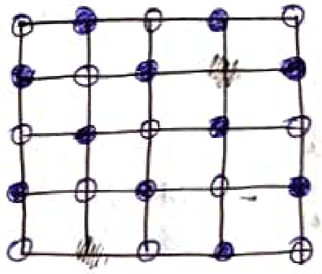
Happen in ceramic and ionic materials



(e) Schottky defect

↳ Electrical neutrality is maintained.

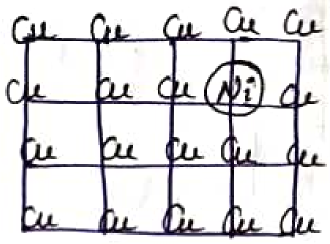
→ Schottky defect in metals = vacancy



Kröger Vink notation for defects

M_s^c , M: type of defect or symbol of the element
S: symbol of normal occupant
C: charge state → x : neutral
• : positive
' : negative

Representation:

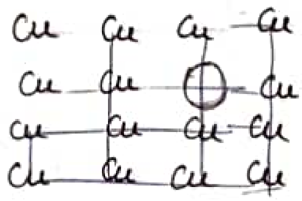
① 

→ M : Ni
S : Cu
C : x

Reaction: $Ni \xrightarrow[\text{matrix material}]{Cu} \underset{\text{substitutional defect}}{\boxed{Ni_{Cu}^{x}}} + \underset{\text{copper in copper material}}{Cu_{Cu}^{x}}$

[Ni substitution in Cu]

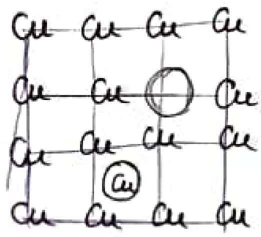
② $V_{Cu}^{x} \xrightarrow{Cu} V_{Cu}^{x} + Cu_{Cu}^{x}$



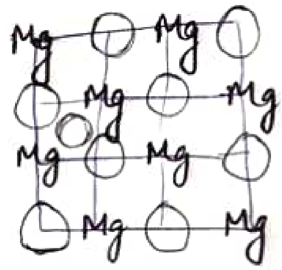
③ null $\xrightarrow{Cu}$ $\underbrace{Cu_i^{x} + V_{Cu}^{x}}_{\text{Frenkel defect}} + Cu_{Cu}^{x}$

at interstitial sites

vacancy defect



④ null $\xrightarrow{MgO}$ $Mg_{Mg}^{x} + \underbrace{O_i'' + V_O^{\bullet\bullet} + O_O^{x}}_{\text{Frenkel defect (oxygen)}}$



⑤ Schottky defect in TiO_2 :

$$null \xrightarrow{TiO_2} V_{Ti}'''' + 2V_O^{\bullet\bullet} + Ti_{Ti}^{x} + O_O^{x}$$

⑥ Doping of CaO in ZrO_2:

$$CaO \xrightarrow{ZrO_2} Ca_{Zr}'' + O_O^{x} + V_O^{\bullet\bullet} + Zr_{Zr}^{x}$$

doping is usually by substitution

from CaO & matrix also

If doping is introduced by interstitial defect:

$$CaO \xrightarrow{ZrO_2} Ca_i^{\bullet\bullet} + O_i'' + Zr_{Zr}^{x} + O_O^{x}$$

⑦ Doping of MgO in NiO :

$$MgO \xrightarrow{NiO} Mg_{Ni}^{x} + O_O^{x} + Ni_{Ni}^{x}$$

⑧ Doping of Al_2O_3 in ZnO :

$$Al_2O_3 \xrightarrow{ZnO} Al_{Zn}^{\bullet} + O_O^{x} + 2O_i'' + Zn_{Zn}^{x} + Al_i^{\bullet\bullet\bullet} + O_O^{x}.$$

$$Al_2O_3 \xrightarrow{2ZnO} 2Al_{Zn}^{\bullet} + 2O_O^{x} + O_i'' + Zn_{Zn}^{x} + O_O^{x}$$

$$Al_2O_3 \xrightarrow{3ZnO} 2Al_{Zn}^{\bullet} + 3O_O^{x} + V_{Zn}'' + Zn_{Zn}^{x} + O_O^{x}.$$

⑨ Doping of ZrO_2 in Y_2O_3:

$$2ZrO_2 \xrightarrow{Y_2O_3} 2Zr_Y^{\bullet} + 3O_O^{x} + Y_Y^{x} + O_i'' + O_O^{x}$$

$$ZrO_2 \xrightarrow{Y_2O_3} Zr_Y^{\bullet} + 2O_O^{x} + V_O^{\bullet\bullet} + V_Y''' + Y_Y^{x}$$

5-06-23

Incorporating ZnO in Al_2O_3

① $\overset{2+}{Zn}O \xrightarrow{Al_2O_3} Zn_{Al}' + V_{Al}''' + O_o^x + 2V_o^{\cdot\cdot}$

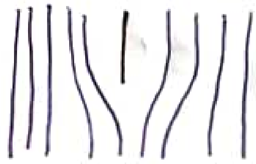
② $2ZnO \xrightarrow{Al_2O_3} 2Zn_{Al}' + 2O_o^x + V_o^{\cdot\cdot}$

③ $3ZnO \xrightarrow{Al_2O_3} 2Zn_{Al}' + Zn_i^{\cdot\cdot} + 3O_o^x$

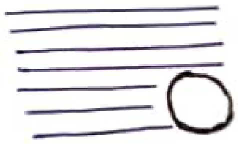
④ $ZnO \xrightarrow{Al_2O_3} Zn_i^{\cdot\cdot} + O_i'' + Al_{Al}^n + O_o^x$

② Line Defects (Dislocation)

ⓐ Screw defect:



ⓑ Edge defect:



③ Surface Defects

↳ On the outermost surface of a solid.

12-06-2023

CERAMICS

↳ A-non-metallic inorganic solid (crystalline material).
(From Greek 'Keramikos': "Fixed clay")

↳ Polycrystalline, inorganic, non-metallic materials that acquire their mechanical strength through a firing or sintering process.

→ Ceramics are used in a wide range of technologies such as refractories, spark plugs, dielectrics in capacitors, sensors, abrasives, etc.

→ The space shuttle makes use of ~25,000 reusable, lighweight, ~~tight~~ highly porous ceramic tiles that protect the aluminium frame from the heat generated during re-entry into the Earth's atmosphere.

Classification:

A. Based on Raw Materials:

① Traditional ceramics: Mainly made from natural raw materials.
Eg, Kaolinite (clay mineral), quartz, feldspar.
↳ $Al_2Si_2O_5(OH)_4$

② Advanced ceramics: Made from artificial or chemically modified raw materials.
Eg, Al_2O_3 ⇝ made from Kaolinite.
↳ most important source of Al.

→ Feldspar
↳ composition: anhydrous aluminosilicate minerals containing K, Na or Ca.
↳ Most important minerals: Orthoclase $K(AlSi_3)O_8$
Albite $Na(AlSi_3)O_8$
Anorthite $Ca(Al_2Si_2)O_8$
↳ Low melting point ~~ceramics~~ provides the fluxing agent during sintering.

→ Kaoline: $Al_2Si_2O_5(OH)_4$.

→ SiC : cutting tool

$$SiO_2 \xrightarrow[220°C]{C} SiC \quad (C = coke)$$

→ TiO_2: toothpaste, paints (white base), coating of tablets
↳ biocompatible material
↳ manufactured from Ilmenite ($FeTiO_3$)
→ black sand.

$$FeTiO_3 + H_2SO_4 \longrightarrow TiOSO_4$$

$$TiOSO_4 \xrightarrow{H_2O} TiO(OH) \xrightarrow{1000^\circ C} TiO_2$$

→ ZrO_2: Zirconia (from Zircone – $ZrSiO_4$)

$$ZrSiO_4 \longrightarrow ZrO_2 + SiO_2$$

B. Functional Classification:

1. Electrical
2. Bio-medical
3. Automobile
4. Aerospace
5. Magnetic ceramics
6. Structural

C. Chemical classification:

1. Oxides: SiO_2, ZrO_2, MgO, NiO, CuO
2. Sulphides: ZnS, BeS
3. Carbides: SiC, WC
4. Nitrides: Si_3N_4, Mg_3N_2.

Processing of Ceramics:

1. Synthesis: Making ceramic powder of required particle size, which is ready for shaping by crushing, grinding, blending with different powders, etc.
2. Green ceramics: shape forming (green = fresh)
3. Sintering: High temperature processing.

Synthesis
↳ Making ceramic powder
↳ Raw material selection criteria
- depends on the properties required for the finished product/ component.
- purity, particle size, reactivity are important criteria.

↳ Purity influence strength and oxidation resistance.
↳ The impurity have effect on mechanical, electrical and optical properties. Eg., doping.

↳ Particle size:
↳ affects particle packing, shrinkage and porosity.
↳ Fine particles (size 1μm) with varying sizes give a dense material.
used in machines (machining doesn't break)
↳ Porous ceramics: thermal ceramics (tiles)
→ thermal conductivity ↓

↳ Reactivity:
↳ compatibility with solvent
↳ Difference in surface free energy → primary driving force towards densification

→ Particle size distribution and reactivity are important in determining the sintering T & time. (eg., finer size can achieve densification in lower T & time).

→ Techniques for Powder Preparation:

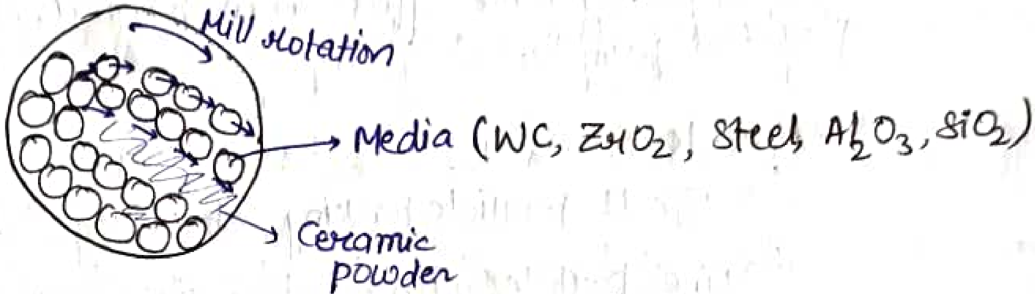
Mechanical	Chemical	Miscellaneous
Screening	Precipitation	Calcining
Ball milling	sol-gel	Combustion
Hammer milling	plasma	
Roll crushing	Hydrothermal	
	Freeze drying	

→ Screening: for getting particular size of particles.

12-06-23

Ball Milling

- Common method for reducing particle size.
- A ball mill is a barrel (usually made of a ceramic) that rotates on its axis and is partially filled with a grinding medium (called media) in the form of spheres, cylinders or rods.
- The media should have a high density for most effective collisions.



- Homogenisation of particle size is possible. (produces broad particle size distribution)
- Disadvantage: Due to media usage, contamination of ceramics is possible.
- Types:

Wet Milling

(lubricants: ethylene glycol, oleic acid, glycerine)

- ~~do~~ sticking is present, no dust
- low powder required
- Homogenisation, high speed
- Better (no problem due to heating)
- smaller particle than dry method
- compatible with spray drying.

Dry Milling

- no separation is required; sticking can be avoided
- avoids drying of the powder
- Less media and lining wear.
- contamination with media is low.
- free-flowing powder

Sol-gel method ⇝ chemical method.

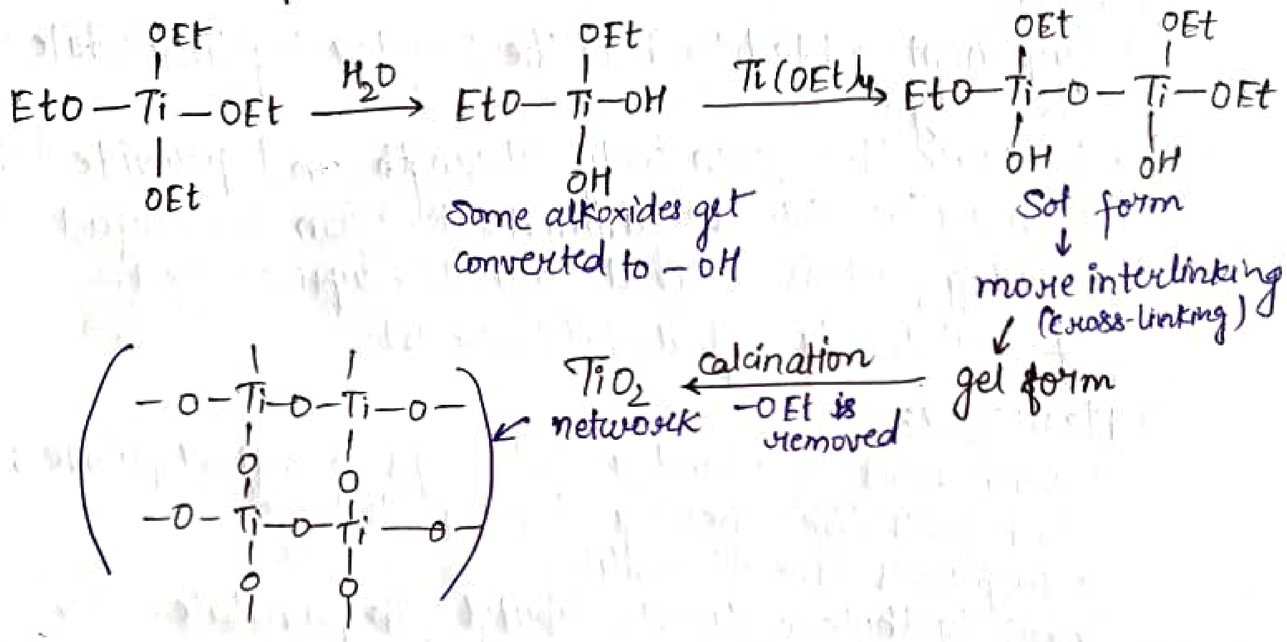
- Sol: Colloidal particles or molecules suspended in a liquid/solution
- Gel: A continuous 3-D network formed by mixing sol with another liquid.
- Used for fabrication of metal oxides, especially SiO_2, TiO_2, etc.
- Starting material: metal alkoxide (eg., $Ti(OEt)_4$)
- SiO_2, TiO_2, ZrO_2 are prepared using this method.

Solution of metal alkoxides $\xrightarrow[\text{condensation}]{\text{Hydrolysis \&}}$ Sol (solution) $\xrightarrow{\text{Gelation}}$ Polymeric gel $\xrightarrow{\text{Drying}}$ Dried gel $\xrightarrow{\text{Firing}}$ Dense product

Steps-involved:

- Form a stable dispersion (sol) of particles (diameter $< 0.1 \mu m$) in a liquid.
- By change of concentration (evaporation of a portion of liquid), aging or addition of a suitable electrolyte, induce polymer-like, 3 D bonding to occur throughout the sol to form a gel.
- Evaporate the remaining liquid from the gel.
- Increase the temp. to convert the dehydrated gel to the ceramic composition.

Eg.



Calcining

↳ High temperature treatment of powder to modify their characteristics.

↳ By calcining; coarsening, decomposition, reacⁿ & dehydration have been possible.

coarsening → crystallite growth or fusing small particles together to form large particles

decomposition → converting composition of carbonate/nitrate to oxides

dehydration → important in preparation of cement & plaster.

Green Ceramics (Green Body)

↳ Shaping methods for ceramic products:

① Powder compaction: dry pressing, hot pressing, cold isostatic pressing, ...

② casting: using a mold containing a liquid or slurry: slipcasting, tape casting, ...

③ Plastic forming: extrusion, injection molding, etc — using ~~pressing~~ pressure to shape the green ceramic.

→ Slurry is a suspension of ceramic particles in a liquid.

→ The green body is strong enough to be handled and machined.

↳ Common additives for ceramic powder during green body formation:

① Binder:

↳ Component added to hold the powder together while shaping the body.

↳ Increase the green body strength and provide lubrication.

↳ We must be able to eliminate it from the compact during the firing process without any disruptive effect.

Eg., water, polyvinyl alcohol (solvents).

② Plasticizer:

↳ component of a binder that keeps it soft or pliable; it improves the rheological properties.

↳ improves the flexibility.

Eg., polyethylene glycol, dibutyl ~~pth~~ phthalate.

→ The distinction b/w binder and plasticizer is sometimes not too clear.

→ Techniques involved in forming ceramic powders into desired shape (green body):

① Uniaxial (Die) pressing:

↳ powder compaction method involving uniaxial pressure applied to the powder placed in a die b/w two rigid punches.

↳ effectively used for mass production of simple parts.

↳ Limited to simple solid shapes, such as flat plates, blocks & cylinders.

↳ cold pressing: Die pressing which is conducted at the room temp.

↳ hot pressing: If the pressing process is conducted at increased T.

↳ Dry pressing: powder containing moisture below 4%.

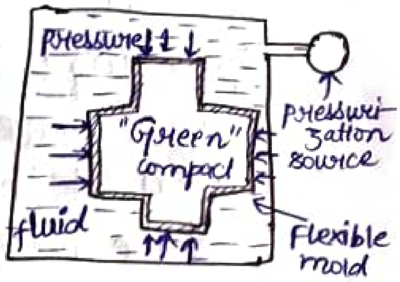
↳ wet pressing: feed powder containing 10–15% moisture content.

↳ Pros: fast production, easy automation, low cost

↳ Cons: Improper density (density variation), die wear, cracking.

② Isostatic pressing:

↳ Powder compaction method involving applying pressing from multiple directions through a liquid or gaseous medium surrounding the compacted part.



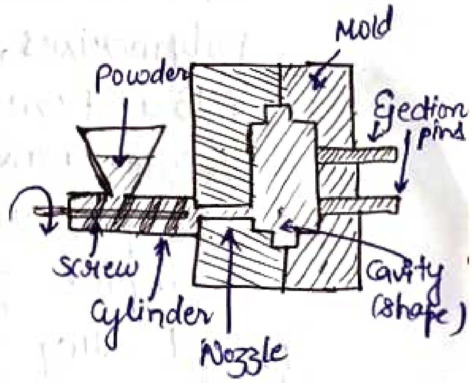
↳ Advantages: • wide range of complex shapes & sizes can be obtained.
• uniform density of the pressed product.
• Low tooling costs.

↳ Disadvantages: • poor dimensional control for complex shapes.
• products often require green machining.
• long cycle times (b/w 5 & 30 min.) give low production rates.
• difficulty in automation.

→ HIP (Hot Isostatic pressing): Involves isostatic pressing conducted at increased temperature. As a pressure medium a gas (N or Ar) is used. This process is called HIPing.
↳ combines pressing & sintering, causing consolidation of powder particles, healing voids and pores.
↳ The part shrinks and densifies, forming sound high strength structure.
↳ Pros: produces dense materials without growing the grains.
↳ Cons: cost.

③ Injection Molding:

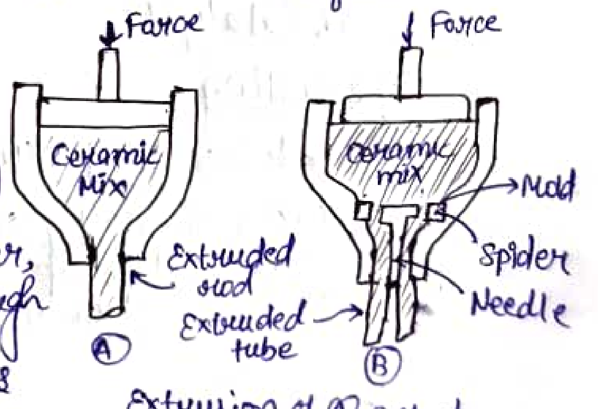
↳ Method of compaction of ceramic powder fed and injected into a mold cavity by means of a screw rotating in cylinder.
↳ widely used for manufacturing small parts having complex shapes.



↳ Limitation: Initial tooling costs of the mold can be quite high (but re-usable)
↳ Incomplete mold filling and solidification defects.

④ Extrusion:

↳ Involves forcing a deformable mass through a die orifice (like toothpaste from a tube).
↳ The ceramic powder mixed with binder, plasticizer & lubricant is passed through the die.
↳ Used for producing ceramic components having a uniform cross-section & a large length-to-diameter ratio (e.g., tubes & rods)



Extrusion of Ⓐ a rod
Ⓑ a tube

↳ Warpage or distortion can occur during drying or firing due to density variations.
↳ Laminations: cracks that generally form a pattern.
↳ Tearing: surface cracks that form as the material exists the extruder.

Slip casting:

↳ Slip is poured into a mold (usually PoP). Water passes via capillary action, into the porous plaster leaving a layer of solid on the wall of the mold. The surplus slip is poured out.
↳ complex shapes (hollow) can be formed.
↳ Molds can be easily formed from plaster of Paris ($2CaSO_4 \cdot H_2O$).
↳ Used for manufacturing fine china, teapots, jugs, sinks, sanitary ware, thermal insulation parts.

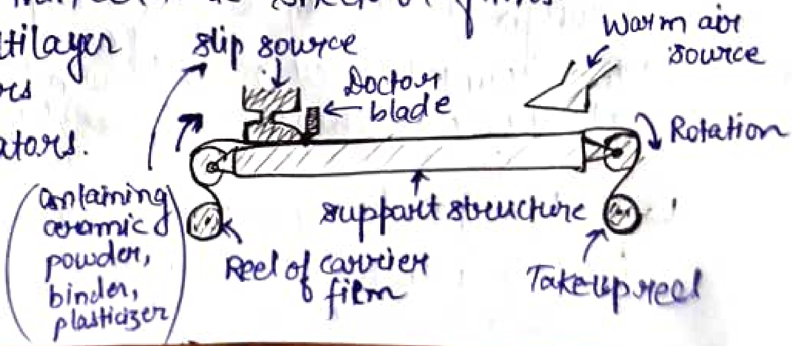
Gel casting

↳ Process of shape forming slurry prepared from ceramic powder mixed with a solution of organic monomer.
↳ When the slurry is poured into ~~the~~ a mold, the monomer polymerises, forming a gel that binds ceramic powder particles into a strong complex-shaped part. The parts may be machined before firing.
↳ The process is economical and used for manufacturing large complex parts (such as turbine rotors).

Eg, gel casting of alumina powder by the in situ polymerisation of acrylamide monomer ($C_2H_3CONH_2$) in the presence of ammonium ~~pers~~ persulfate ($(NH_4)_2S_2O_8$) initiator & tetramethylethylmediamine as catalyst.

Tape casting

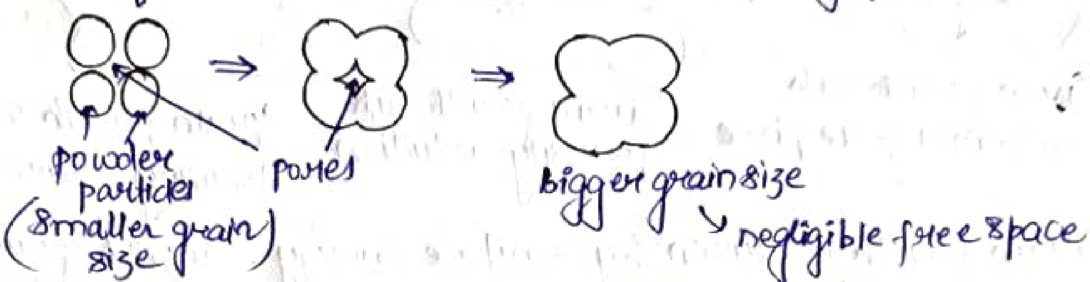
↳ Used for preparing thin ceramic sheets or films.
↳ for manufacturing multilayer ceramics for capacitors and dielectric insulators.



Sintering

↳ Thermal treatment of a powder or green compact at a temp. below the melting point of the main ~~component~~ constituent, for the purpose of increasing its strength by bonding together of the particles.
(Densification of particulate ceramic compact)

↳ Determines final mechanical properties of any product.

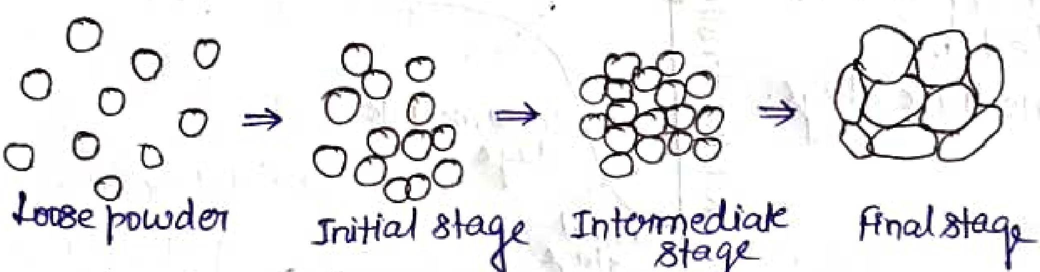


↳ Strength ↑ by bounding together of the particles.

↳ Primary mechanism for material transport : diffusion & viscous flow.

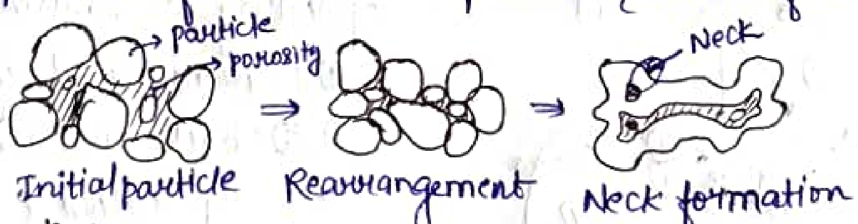
Stages of Sintering:

- Initial
- Intermediate
- Final.



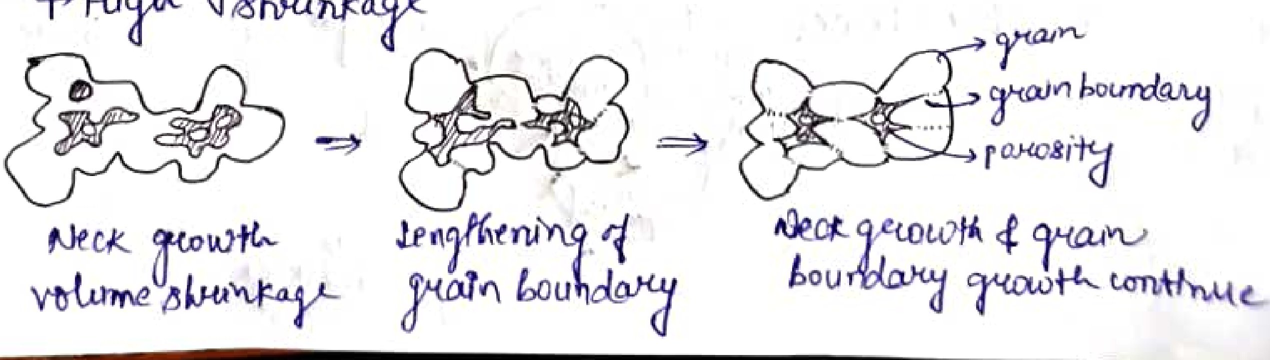
① **Initial stage:** Density: 60%-65%.

- Rearrangement ⇝ more no. of contact
- Neck formation ⇝ particles start to fuse



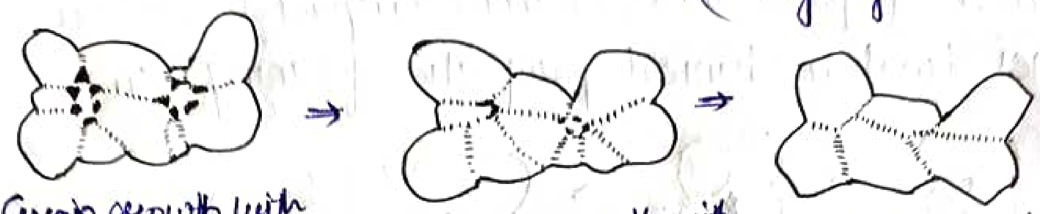
② **Intermediate stage:** Density = 65% – 90%

- Neck growth (Porosity decreases)
- Grain growth
- High shrinkage



③ Final Stage: Density = 90% - 95%

- → Much grain growth
- → Discontinuous pore phase
- → Grain growth with porosity elimination (through grain boundaries, diffusion of grain)



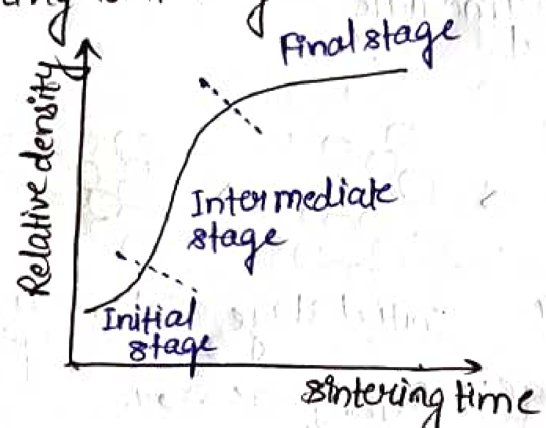
Grain growth with discontinuous pore phase → Grain growth with porosity reduction → Grain growth with porosity elimination

→ Grain growth is driven by surface energy. Curved grain boundaries ~~much~~ move in such a way that then gain a larger radius of curvature (i.e., straighten out).

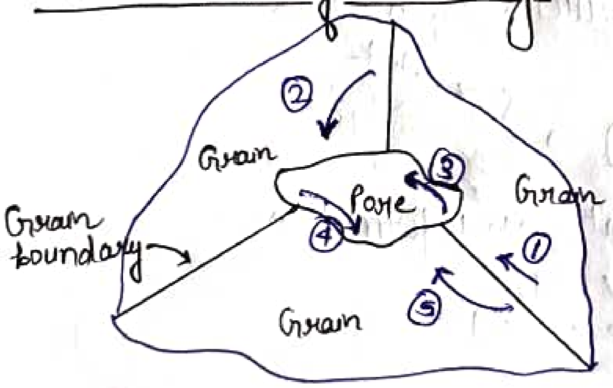
→ Binders and plasticizers will be removed in initial and intermediate stages.

→ Density variation during sintering:

↳ The density increase is highest in intermediate stage.



- Mechanisms of Sintering:

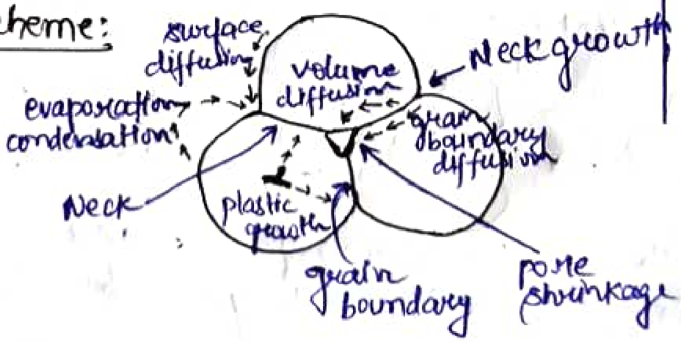


Operating mechanism:

①: Grain boundary diffusion
②,⑤: bulk diffusion
④: evaporation & condensation
③: surface diffusion

Densification: ①,②,⑤
Supports but doesn't contribute to densification: ③,④

→ Another scheme:



→ Diffusion takes place b/c of higher energy of particles.

Advantages of Sintering:

① Possibility of very high purity for the materials and their great uniformity.

② Absence of segregated particles and inclusions (as often occurs in melt processes).

③ No requirement for deformation to produce directional elongation of grains.