Chapter 3

Crystal and Amorphous Structure in Materials

材料中晶體與非結晶體的結構

Crystal:結晶體

Amorphous:非結晶體

Structure:結構

Materials:材料

- **The space lattice and unit cell： 空間格子與單位晶胞**

原子或離子的排列方式在三維座標上不斷重複，此即 **crystal structure (結晶結構)**。

- Space lattice：空間格子

結晶中的原子排列以三維座標的直線網路交點予以描述。

- **Lattice：單位格子**

以a,b,c 表示三個格子向量，**α, β, γ**為其夾角。

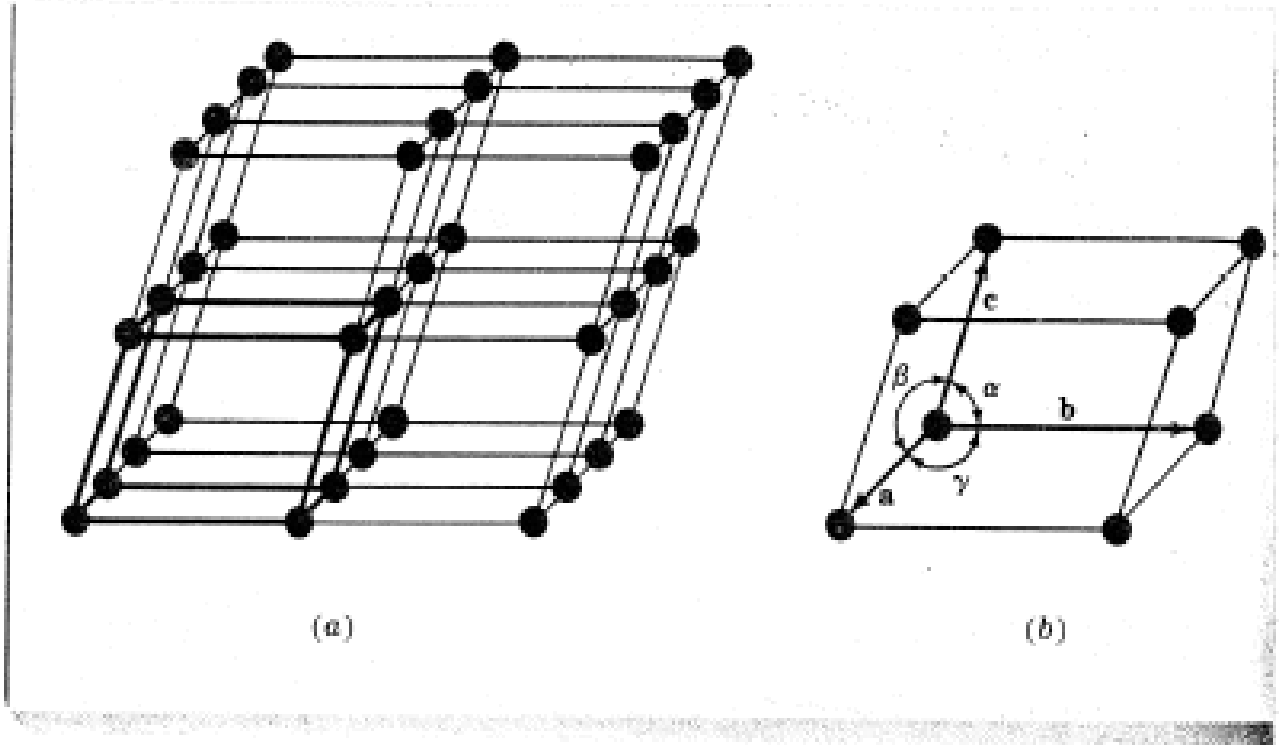


FIGURE 3.1 (*a*) Space lattice of ideal crystalline solid. (*b*) Unit cell showing lattice constants.

七大晶系(Crystal system) and 14 Bravais lattice (布拉格晶群)

Table 3.2 The 14 Bravais conventional unit cells groups according to crystal system.

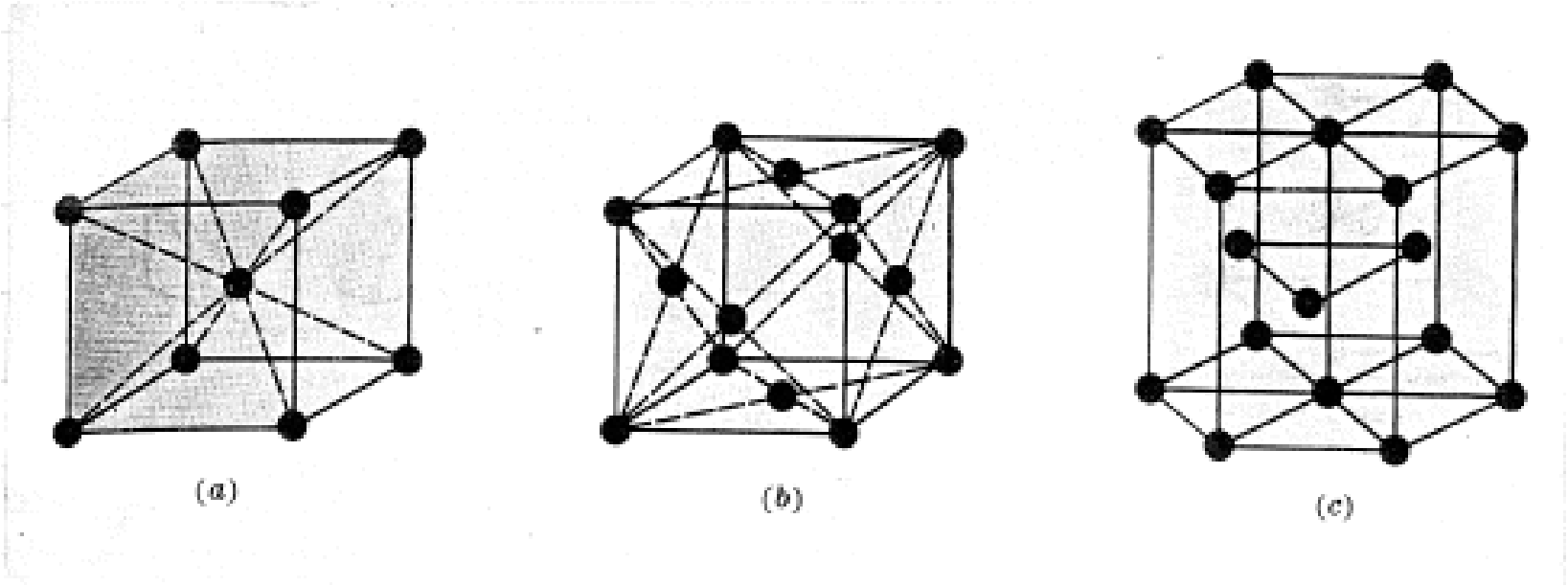
Classification of Space Lattices by Crystal System

Crystal system	Axial lengths and interaxial angles	Space lattice
Cubic 立方	Three equal axes at right angles $a = b = c, \alpha = \beta = \gamma = 90°$	Simple cubic Body-centered cubic Face-centered cubic
Tetragonal 正方	Three axes at right angles, two equal $a = b \neq c, \alpha = \beta = \gamma = 90°$	Simple tetragonal Body-centered tetragonal
Orthorhombic 斜方	Three unequal axes at right angles $a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Simple orthorhombic Body-centered orthorhombic Base-centered orthorhombic Face-centered orthorhombic
Rhombohedral 菱方	Three equal axes, equally inclined $a = b = c, \alpha = \beta = \gamma \neq 90°$	Simple rhombohedral
Hexagonal 六方	Two equal axes at 120°, third axis at right angles $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	Simple hexagonal
Monoclinic 單斜	Three unequal axes, one pair not at right angles $a \neq b \neq c, \alpha = \gamma = 90° \neq \beta$	Simple monoclinic Base-centered monoclinic
Triclinic 三斜	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	Simple triclinic

Principal Metallic Crystal Structures

大多數金屬的堆積有下列三種:

- Body-centered cubic (**BCC**) 體心(a)
- face-centered cubic (**FCC**) 面心(b)
- hexagonal closed-packed (**HCP**) 六方最密堆積(c)



BCC

- Body-centered cubic (BCC)： Crystal Structure 中心原子被**8個最靠近的原子**所包圍，其配位數(coordination number)為 8，單位晶胞內有2個原子。

1 + (1 / 8) × 8 = 2 個原子

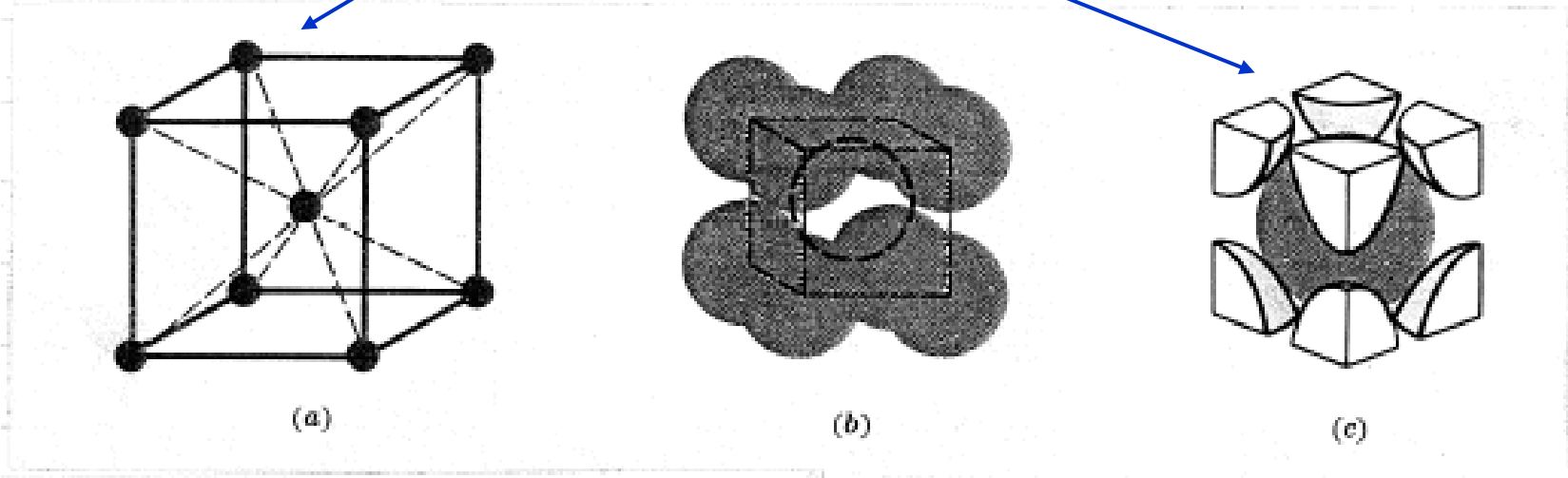
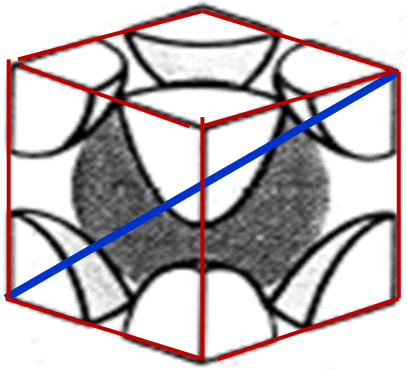
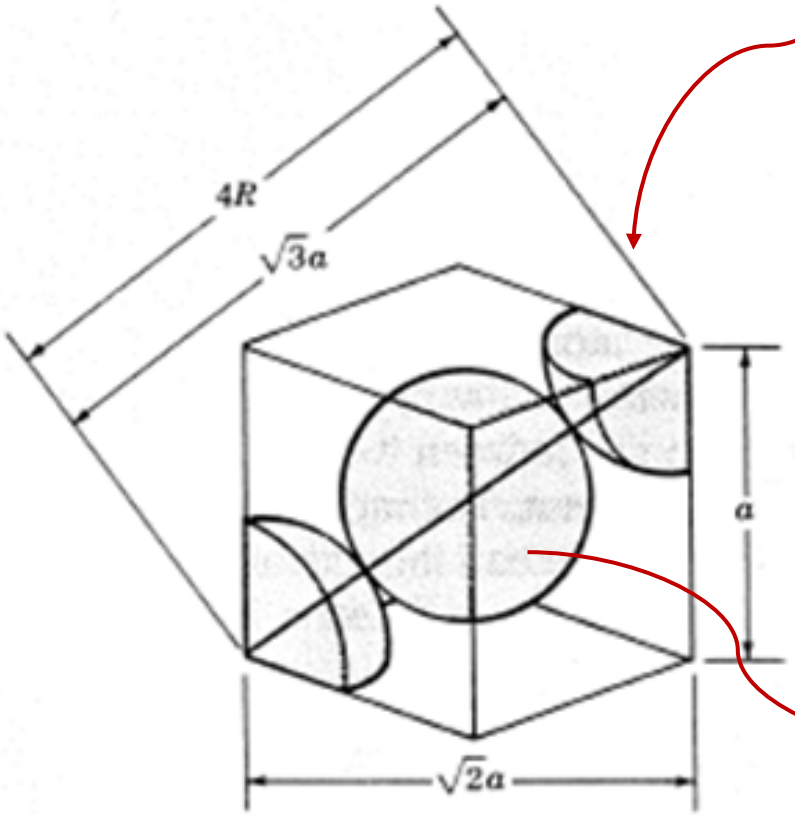


示意圖　　理想圖 (近乎實際)　　單位晶胞示意圖



(c)



$\sqrt{3}a = 4R$

由左圖知：體對角線

$$\sqrt{3}a = 4R$$

$$a = \frac{4R}{\sqrt{3}}$$

體心的中心原子被八個頂角的原子均勻夾住。

〈Ex3.1〉Fe is BCC with atomic radius 0.124 nm.
Calculate the lattice const a ?

Fe 是 BCC，原子半徑為 0.124 nm， 計算晶格常數 a ?

Ans：

In the BCC unit $\sqrt{3}\,a = 4R$

$\sqrt{3}\,a = 4*0.124$

$a = 0.2864$ nm

atomic packing factor (APF) 原子堆積因子

$$APF = \frac{volume \text{ of atoms in unit cell}}{\text{volume of unit cell}}$$

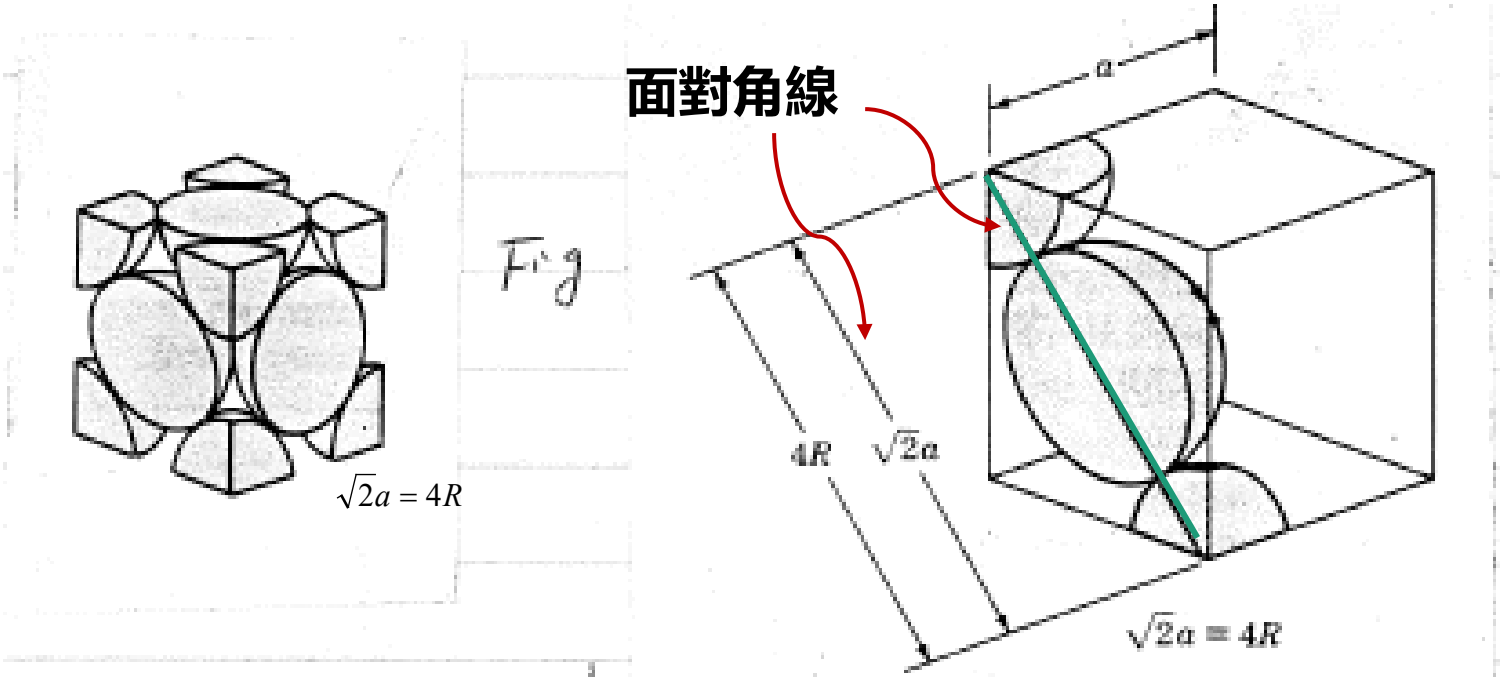
〈 Ex3.2 〉 Calculate the APF for the BCC?

$$APF = \frac{2 * \frac{4}{3}\pi R^3}{a^3}$$

$$\sqrt{3}a = 4R \qquad a = \frac{4R}{\sqrt{3}}$$

$$APF = \frac{\frac{8}{3}\pi R^3}{(\frac{4R}{\sqrt{3}})^3} = 68\%$$

Face-centered cubic (FCC) Crystal Structure
面心結晶結構

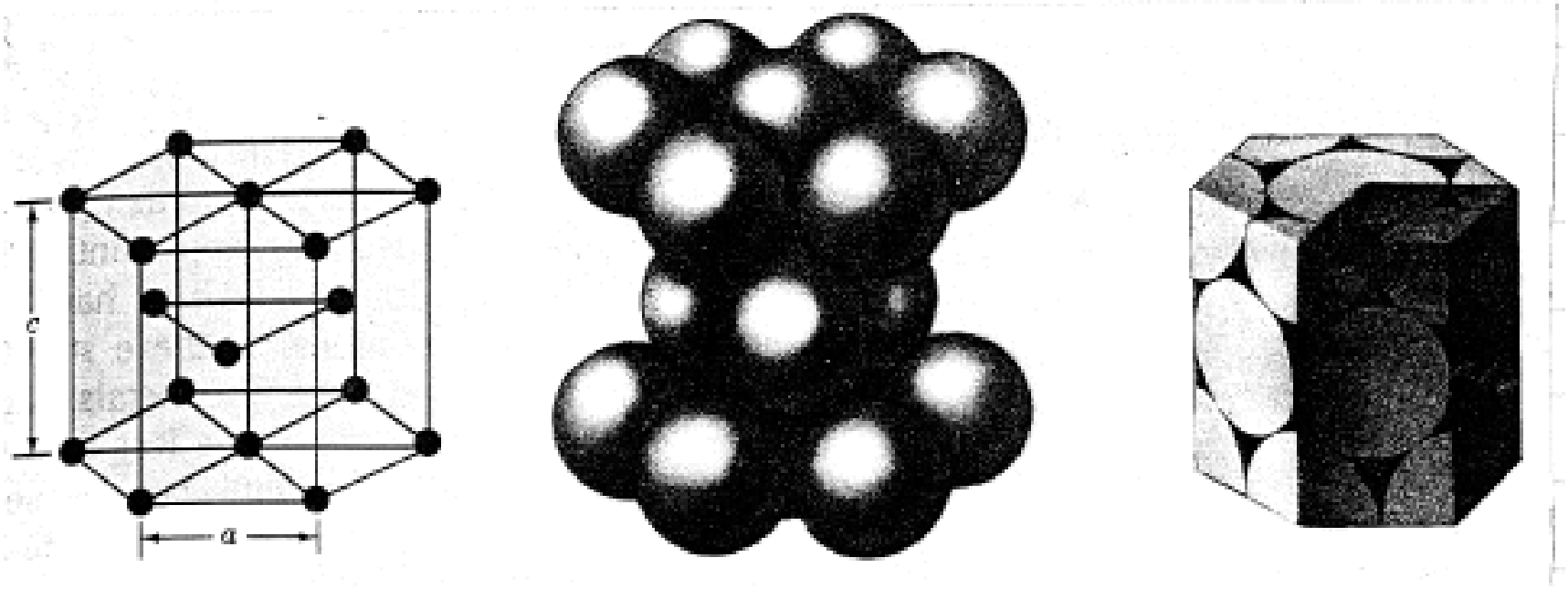


每單位晶胞內有4個原子，coordination number (配位數)為12, 許多金屬 如：Al , Cu, Pb, Ni 等為 FCC

結構由圖知：$\sqrt{2}a = 4R$

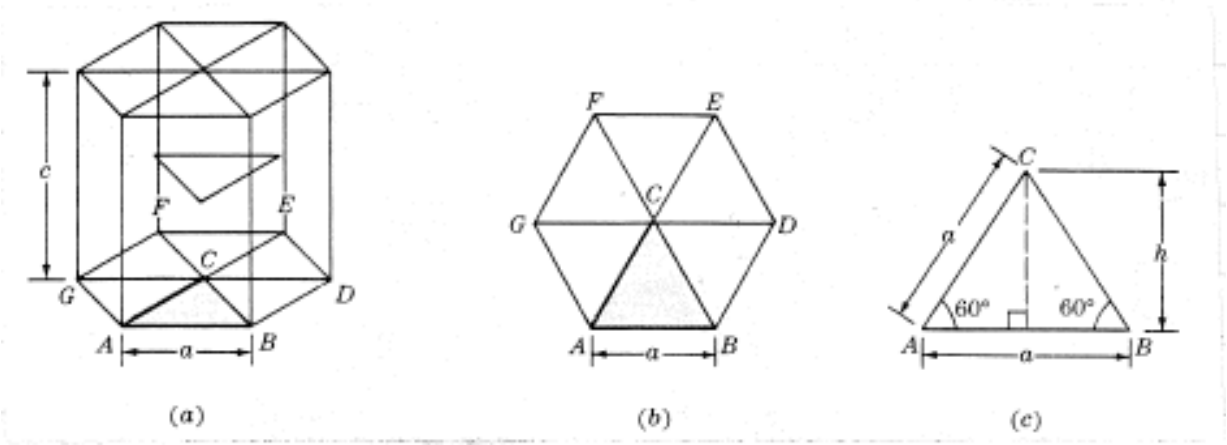
hexagonal close-packed (HCP) Crystal Structure
六方最密堆積結晶結構

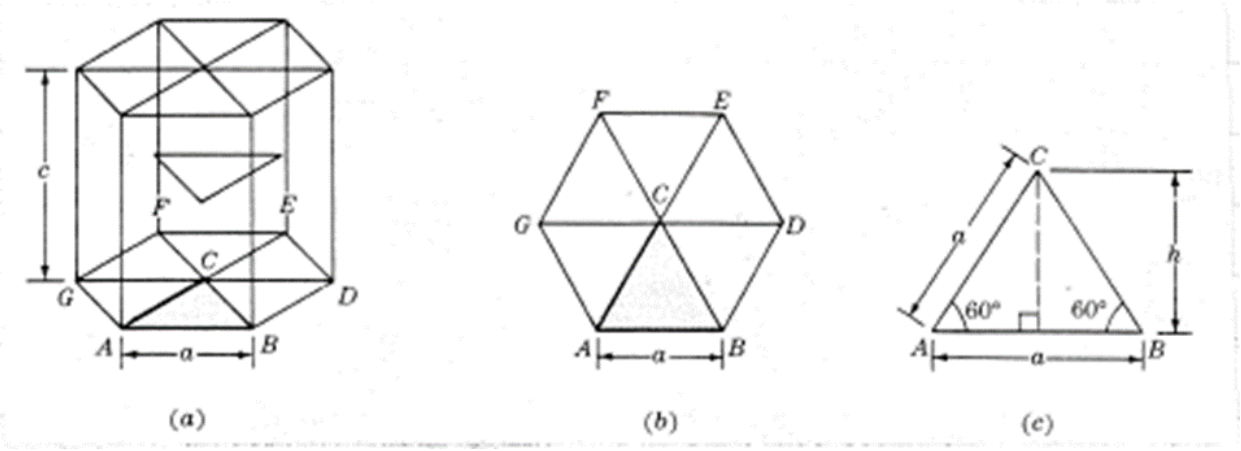
FCC與HCP之APF相同為0.74，由圖知其coordination number為12



〈Ex3.3〉 Calculate the volume of the zinc crystal structure unit cell by using the lattice constants a = 0.2665 nm & c = 0.4947nm

使用晶格常數 a = 0.2665 nm & c = 0.4947nm 計算鋅晶體結構晶胞的體積





$$a = ABC = \frac{1}{2} * a * a \sin 60^\circ = \frac{1}{2} a^2 \sin 60$$

$$HCP\square\ \square\ \square = 6 * \frac{1}{2} a^2 \sin 60 = 3a^2 \sin 60$$

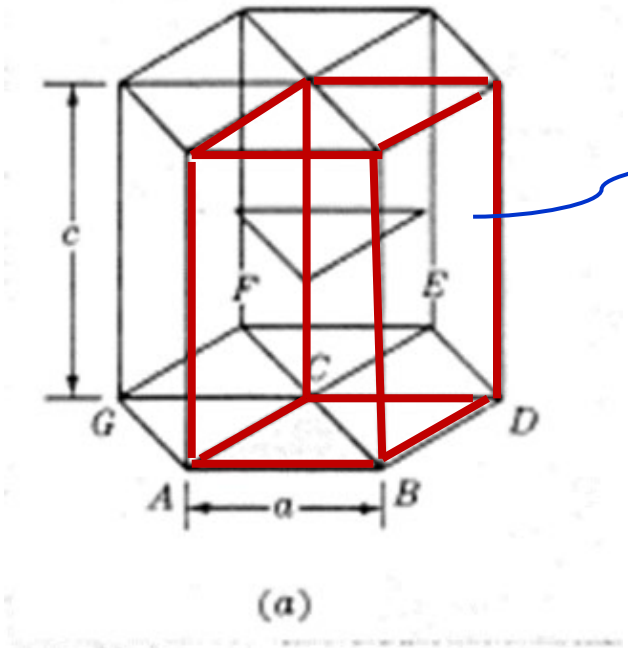
$$volume \text{ of unit cell}$$

$$= (3a^2 \sin 60) * C$$

$$= 3 * 0.2665^2 * 0.866 * 0.4947$$

$$= 0.0913 \text{ nm}^2$$

有些教科書以此為HCP單位晶胞稱為較大晶胞(Larger cell)



1/3 個六方晶的體積, 本教科書是為一最小晶胞

New: Total area of HCP base area ABDC volume of HCP unit cell

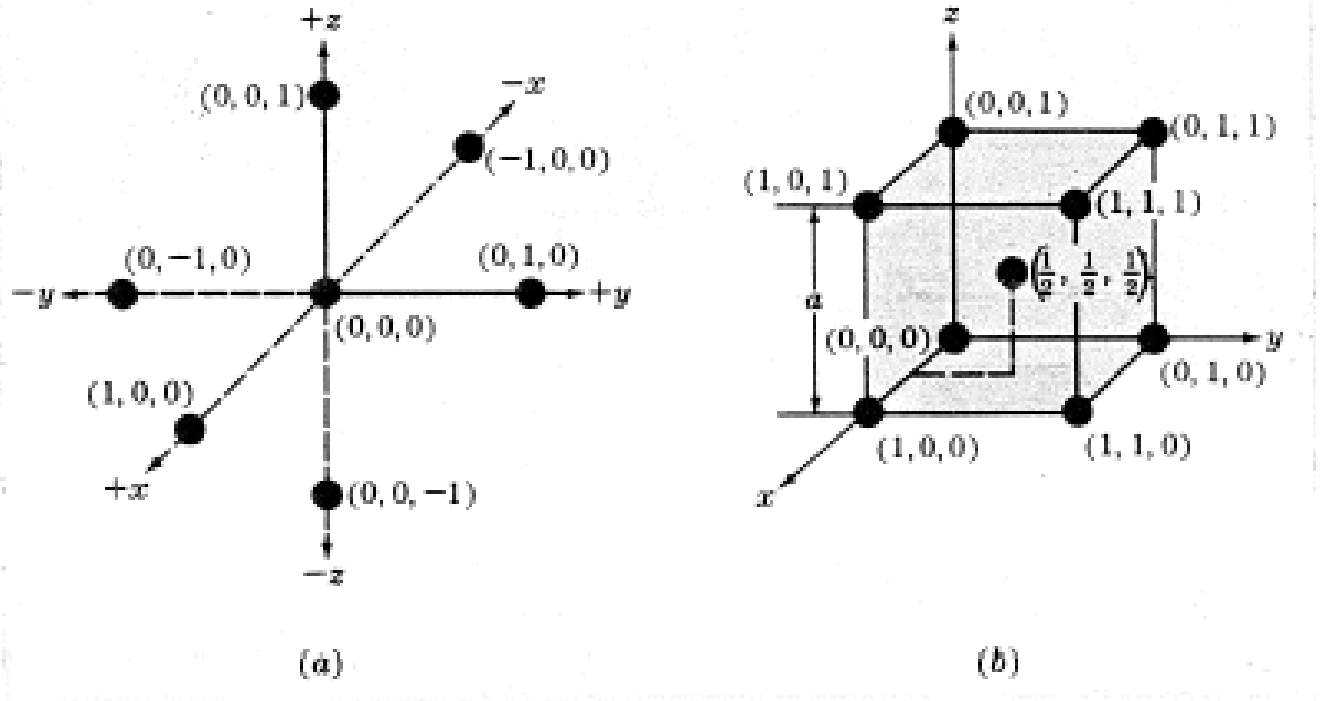
$= (a^2 \sin(60) \times c)$

$= 0.26652 \times 0.866 \times 0.4947$

$= \mathbf{0.0304\ nm^3}$

Atom positions in Cubic unit cell

如圖直角座標及BCC中的原子位置



8個頂點的坐標 (0,0,0) (1,0,0) (0,1,0) (0,0,1) (1,1,1) (1,1,0) (1,0,1) (0,1,1)

中心原子的位子 $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

只以(0,0,0) $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ 二個原子表示BCC之原子位置

Directions in cubic unit cells 立方單位晶胞的結晶方向

結晶方向指數是將方向向量分解成 x, y, z 的分量，再取**最小整數比**。

由單位晶胞的角落當原點，至表面為止。

- [UVW]：表示方向指數的 x, y, z方向，若沿著某些方向上，其原子間的距離都相同，這一組方向稱為 crystallo-graphically equivalent (**結晶等效)**
- 如：< > 為集合

如(a)中方向相量 OR 其終點為(1, 0, 0) 方向指數為[100] (direction Indices)

(c) 中OM 的終點為文(1, ½, 0), 方向指數為
[210]

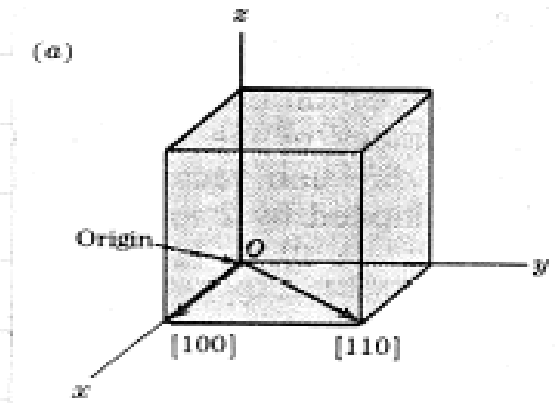
(1,1/2, 0) 終點⇒direction Index [210] 最小整數比 smallest Integers ratios

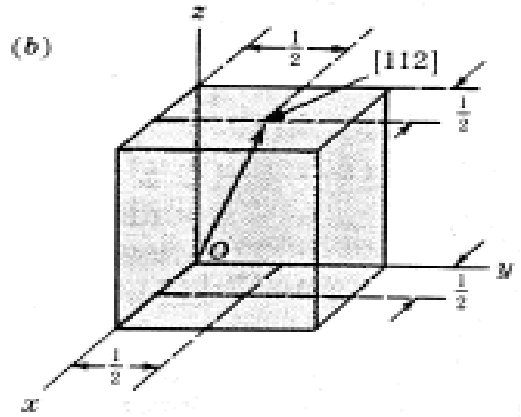
[UVW]：表示方向指數的 x, y, z方向，若沿著某些方向上，其原子間的距離都相同，這一組方向稱為 crystallo-graphically equivalent (**結晶等效**)

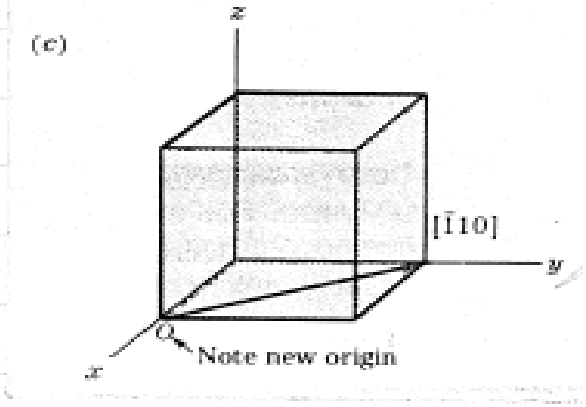
如：< > 為集合

〈Ex3.4〉Draw the following direction vectors in cubic unit cell. 繪製以下立方晶胞之方向向量。 (a) [100] and [110] (b) [112] (c) [10]

Ans:







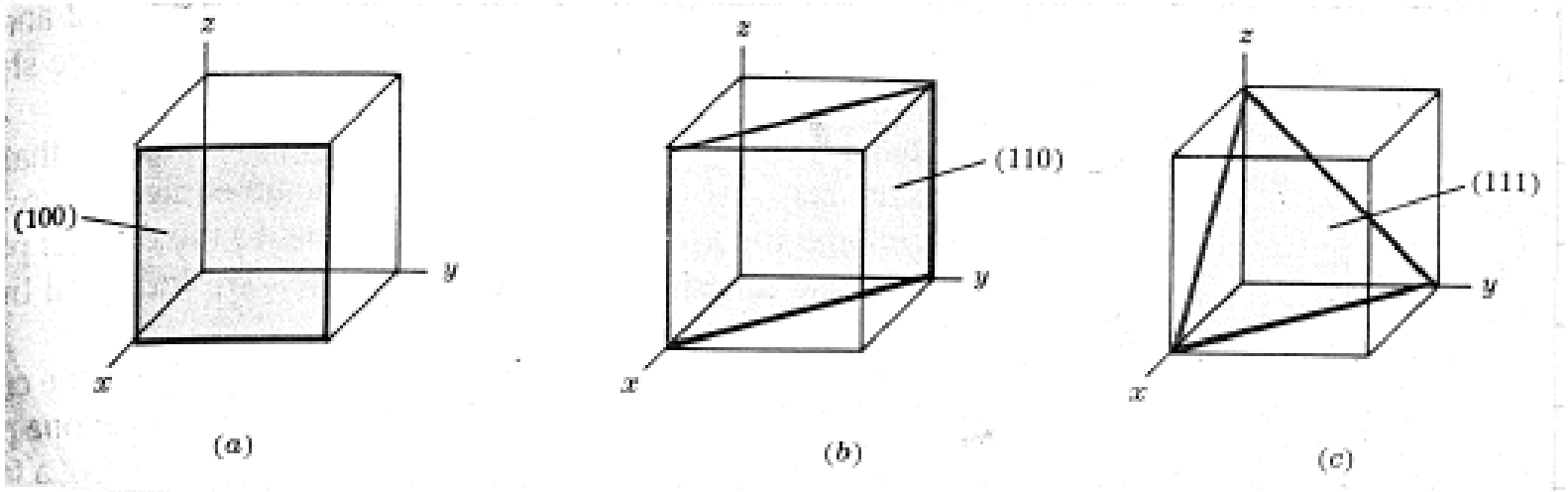
Miller Indices for Crystallographic Planes in cubic Unit Cells (結晶面的米勒指標)

Miller Notation System：立方結晶構造中結晶面之示法，即結晶面與x, y, z 軸的相交**截距的倒數簡單整數比**。

求法：

1. 選一不通過原點(0,0,0)的平面
2. 求此平面與x y z 軸的截距 (平行為 ∞)
3. 求**各截距的倒數**
4. 以 (h k l) 表式 Miller Indices

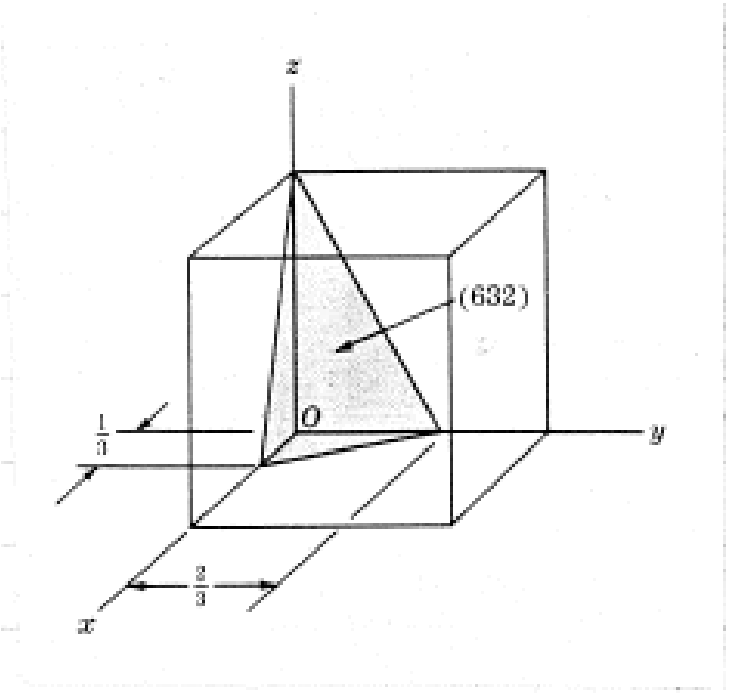
Examples (例) for Miller Indices



(1/1, 1/∞, 1/∞)
⇒ **(100)**

(1/1, 1/1, 1/∞)
⇒ **(110)**

(1/1, 1/1, 1/1)
⇒ **(111)**



(1/(1/3), 1/(2/3), 1/1)

⇒ **(3, 3/2, 1)**

⇒ **(hkl) 為 (632)**

最小整數比

因晶體對稱而等效的一組平面以**{ h k l }**表示，

如(100), (010), (001)同屬於{100 }**平面族**, 稱為

planes of a family or form

Ex3.7> Draw the following crystallographic planes in cubic unit cells

(a) (101) (b) $(1\bar{1}0)$ (c) (221) (d) Draw a (110) plane in a BCC, list the position coordinates of the atoms whose center are intersected by this plane.

Ans：

(a) (101) Miller 倒數為 1,∞,1 與 x, z 交於 1 與 y 平行

(b) $(1\bar{1}0)$ Miller 倒數寫 1,-1,∞ 與 x, y 交於 1, -1 與 z 平行

(c) (221)之 Miller 倒數為 $\frac{1}{2},\frac{1}{2},1$ 與 x, y, z 三軸分別交於 $\frac{1}{2},\frac{1}{2},1$

Ex 3.7 Draw the following crystallographic planes in cubic unit cells. (a) (101) (b) $(1\bar{1}0)$ (c) (221).

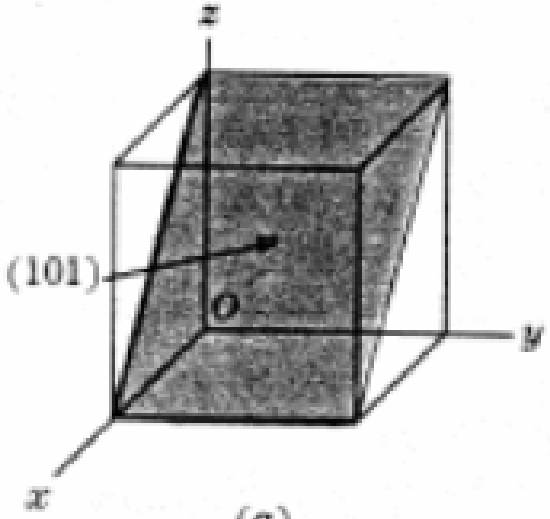
在立方晶胞中畫出下列晶面。

Ans：

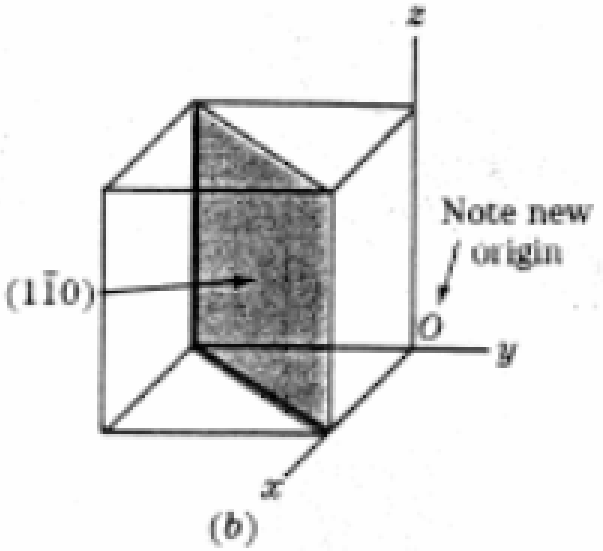
(a) (101) Miller 倒數為 1,∞,1 與 x, z 交於 1 與 y 平行

(b) $(1\bar{1}0)$ Miller 倒數寫 1,-1,∞ 與 x, y 交於 1, -1 與 z 平行

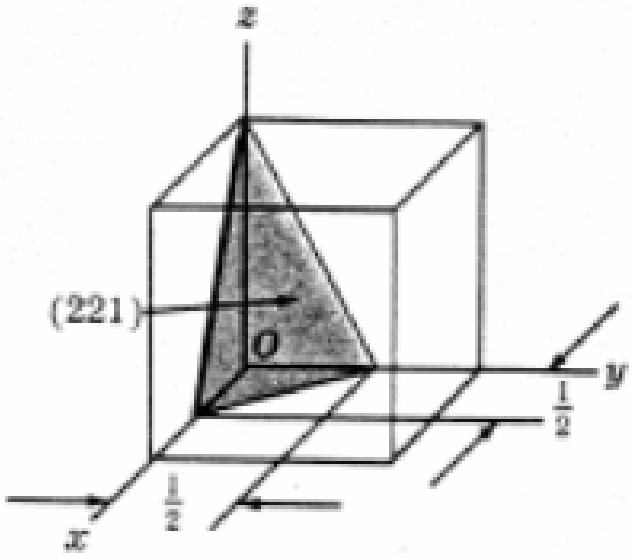
(c) (221)之 Miller 倒數為 $\frac{1}{2},\frac{1}{2},1$ 與 x, y, z 三軸分別交於 $\frac{1}{2},\frac{1}{2},1$



(a)



(b)



(c)

- In cubic crystal structure the interplanar spacing between two closest parallel planes with the same Miller Indices is designated $\mathbf{D_{hkl}}$ **(如下實際TEM穿透式電子顯微鏡)**
- 在立方系統中，結晶面的 Miller Indices 與垂直於它的方向之方向指標是相同的，如[100]方向為垂直於(100)結晶面。

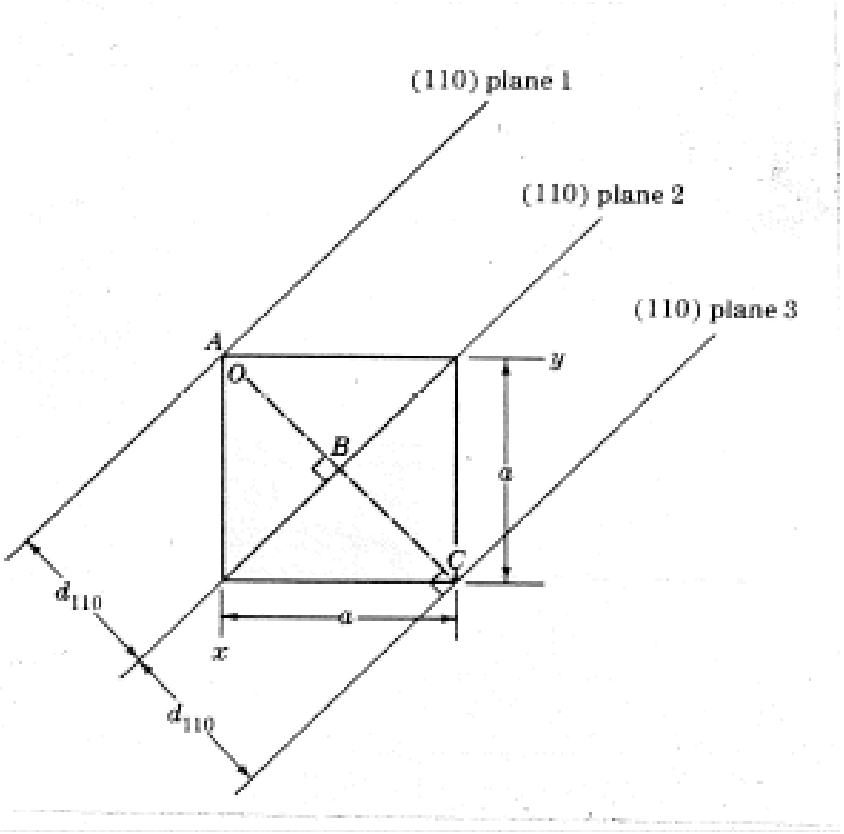
在立方系統中，結晶面的 Miller Indice 與垂直於它的方向之方向指標是相同的，如[100]方向為垂直於(100)結晶面。

立方體間，兩個最接近且平行的平面間距d_{hkl}

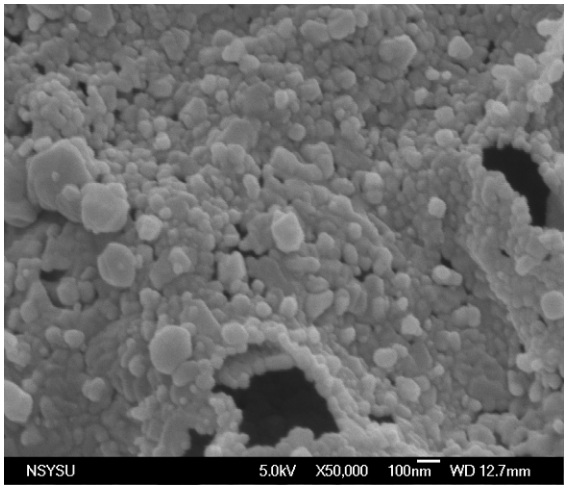
$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

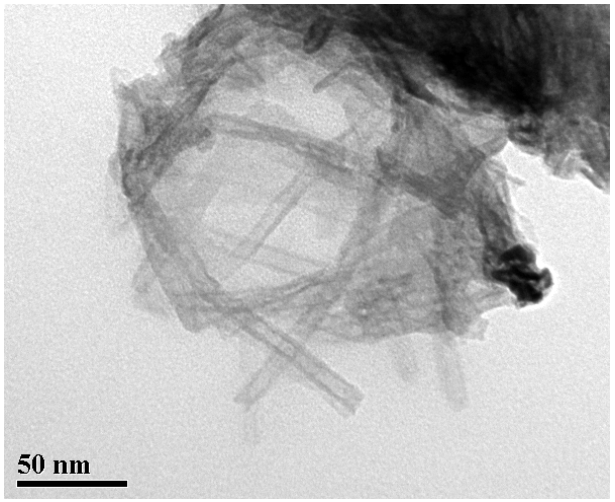
d_{hkl}：相同h,k,l Miller Indice的兩最接近平面之距離

a：lattice constant (edge of unit cube)



- **SEM**: scanning electron microscopy 掃描式電子顯微鏡

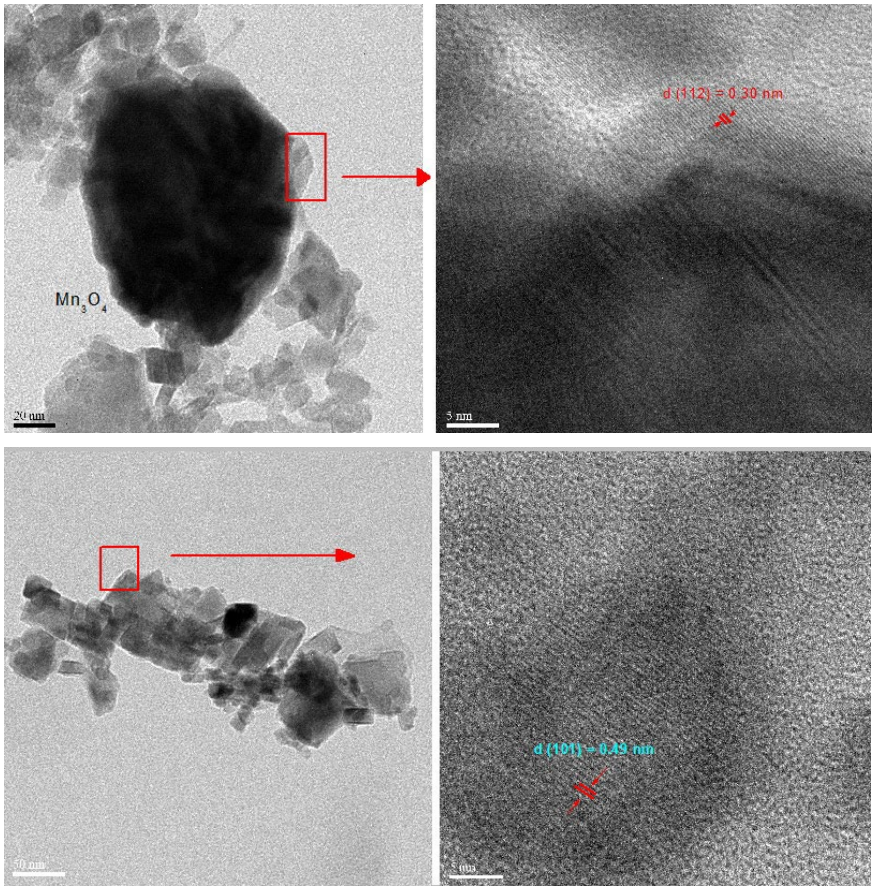




- **TEM**: transmission electron microscopy
  穿透式電子顯微鏡

右圖 2 cm (電腦螢幕上) 相當50 nm, 放大倍率???

2 cm/50 nm = 400,000倍



不同熱處理溫度製備Mn_3O_4之TEM分析
(a-b)室溫、(c-d)100 °C

◆右圖 3 cm (電腦螢幕上)

相當5 nm, 放大倍率???

3 cm / 5 nm = **6,000,000**倍

◆ 左圖 2 cm (電腦螢幕上)

相當20 nm, 放大倍率???

2 cm / 20 nm = **1,000,000**倍

〈Ex3.10〉Copper has an FCC crystal structure and a unit cell with a **lattice constant** of 0.361 nm. What is its **interplanar spacing d_{220}** ?

銅具有 FCC 晶體結構和晶格常數為 0.361 nm 的晶胞。它的**面間距d_{220}**是多少?

Ans:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

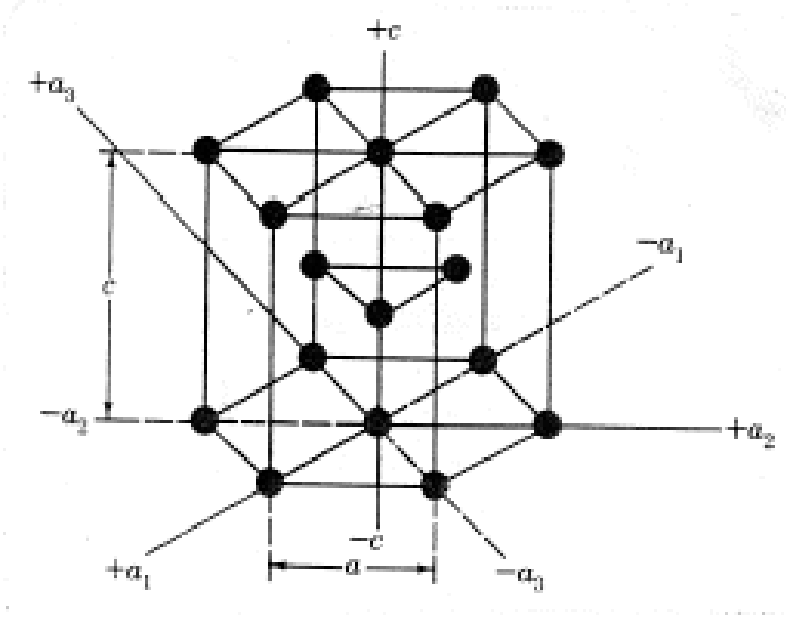
$$= \frac{0.361\,\text{nm}}{\sqrt{(2)^2 + (2)^2 + (10)^2}}$$

$$= 0.128\,\text{nm}$$

Crystallographic Planes and Directions in Hexagonal Unit Cell 六方晶系

- Indices for crystal plane in HCP unit cell

HCP 通常以**4個Miller Indice (h k i l)**表示如圖a_1, a_2, a_3 位於同一平面且夾角為120°**第4軸 C軸是立於單位晶胞中心的垂直軸與C軸的截距的倒數**可得 **i** 指標

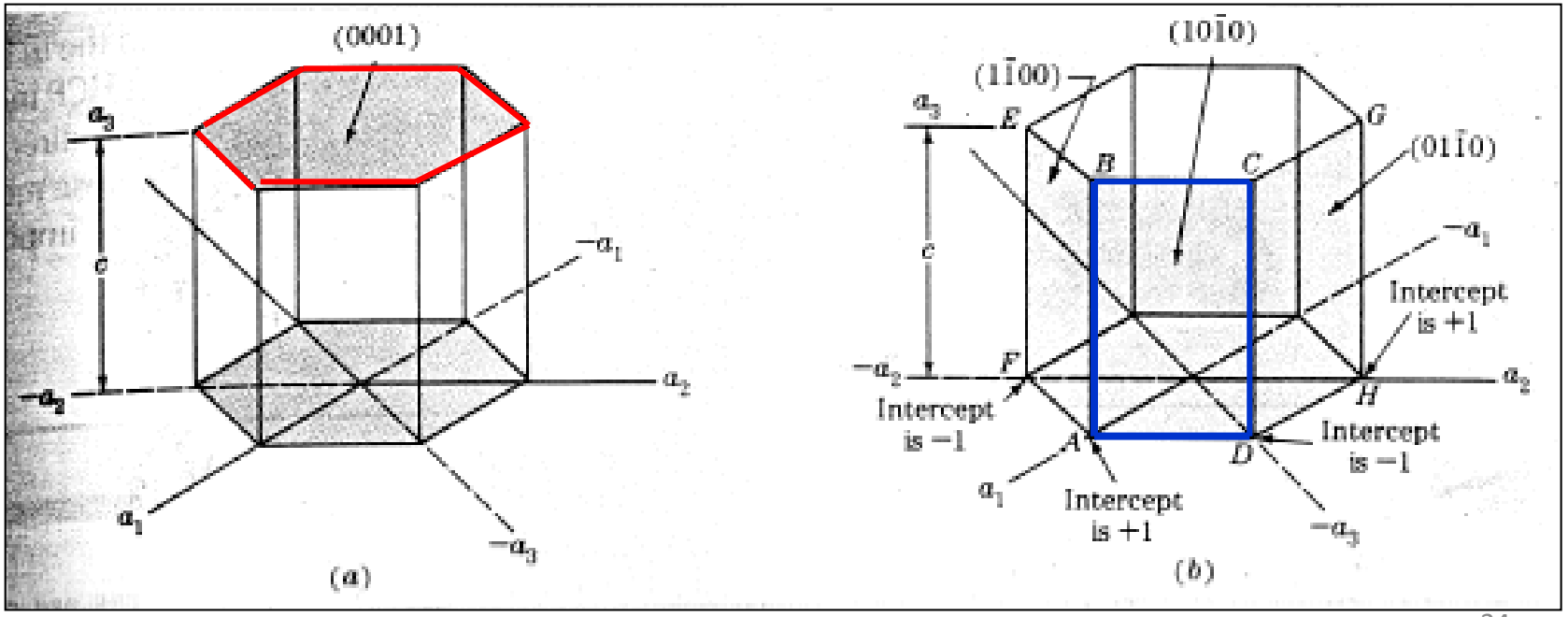


Based Planes (基面)

位於頂層的基面(based plane)和a_1, a_2, 及a_3軸平行, 其截距為$a_1=\infty$,$a_2=\infty$,$a_3=\infty$ C軸截距為1

Miller Indices of based plane (HCP)

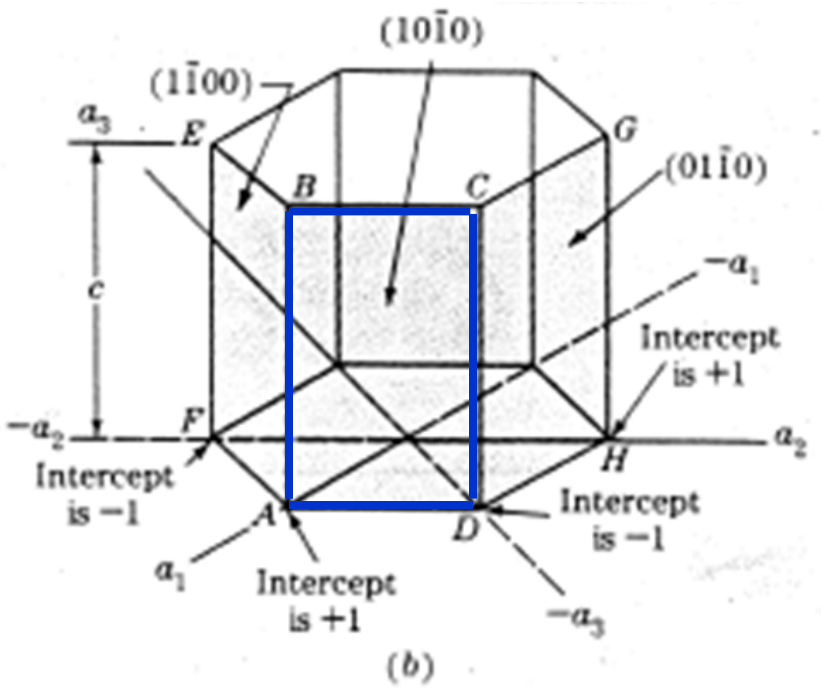
h=0 , k=0 , i=o 及 l=0 , 即 (0001) 面



Prism Plane 菱柱面

上圖(**ABCD**) 的截距為a1 = +1, a2 = ∞, a5 = -1 及 c = ∞

取倒數 h = 1, k = 0, i = -1, l = 0 或 (10$\bar{1}$0), 同理 ABEF 之Miller Indice (1$\bar{1}$00)



Volume, Planar, and linear density Unit-Cell Calculation

- volume density 體積密度
- volume density of Metal

$$\rho_r = \frac{mass/unit\ \text{cell}}{volume/unit\ \text{cell}}$$

以單位晶胞為基準

基礎: 密度 = 質量 / 體積

〈Ex3.11〉 Cu has an FCC crystal R=0.1278 nm. Calculate a theoretical density in **mega**gram (**M**g) per cubic meter (Cu =63.54 g/mole)

Ans：

For FCC $\sqrt{2}a = 4R$

$$\sqrt{2}a = 4*0.1278 \qquad a = 0.361\text{nm}$$

$$\rho_v = \frac{4*\frac{63.54}{6.02*10^{23}}g}{(0.361*10^{-7})^3} = 8.98\,\text{g/cm}^3$$

$$= 8.98\frac{Mg}{m^3} \qquad M:10^6$$

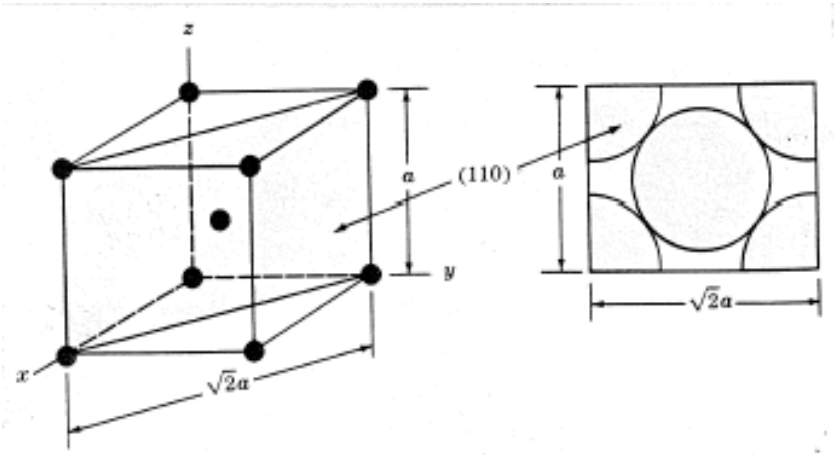
Planar atomic density 晶面原子密度

$$\rho_p = \frac{eqniv.\,\text{no. of atoms whose centers are intersected by selected ared}}{selected\ \text{area}}$$

原子中心在特定區域上的等效原子數

〈Ex3.12〉Calculate the planar atomic density ρ_P on the （110）plane of Fe BCC lattice in atoms per square millimeter (mm), a=0.287 nm.

計算Fe BCC晶格（110）面上的平面原子密度ρ_P，單位為原子/平方毫米（mm），a=0.287 nm。



Ans：

BCC 單位晶胞中（110）面上的等級原子數

$$1+4\times\frac{1}{4}=2$$

$$(\sqrt{2}a)(a)=\sqrt{2}a^2$$ （110）面之 area

$$\rho_P=\frac{2\text{atom}}{\sqrt{2}(0.287)^2}=\frac{17.2\text{atoms}}{\text{nm}^2}$$

$$=\frac{17.2\text{atoms}}{\text{nm}^2}\times(10^6\ \text{nm}/1\ \text{mm})^2$$

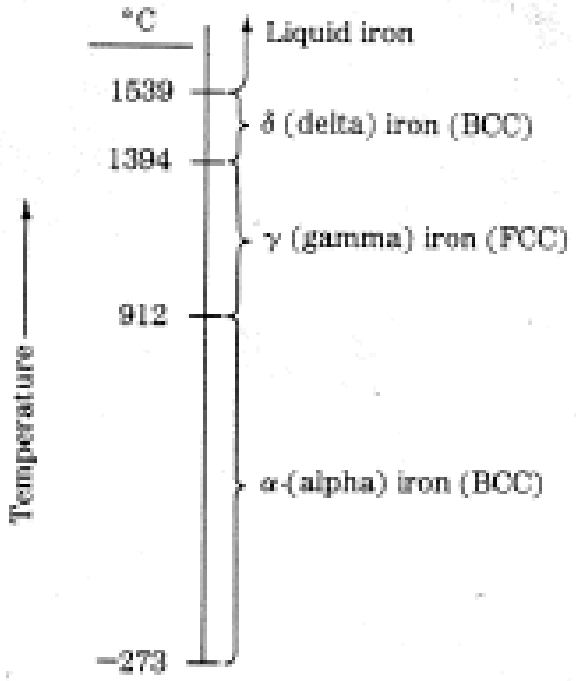
$$=1.72\times10^{13}\ \text{atom}/\text{mm}^2$$

linear atomic density, ρ_l length of line in direction of interest

$$\rho_l = \frac{\text{no. of atomic diam. intersected by selected}}{\text{selected length of line}}$$

原子直徑在特定直線上的原子數

Polymorphusm or Allotropy 多型性或同素異形同一元素或化合物在不同的T.P. 下會有不只一種結晶形式稱之，如Fe：打鐵的意義

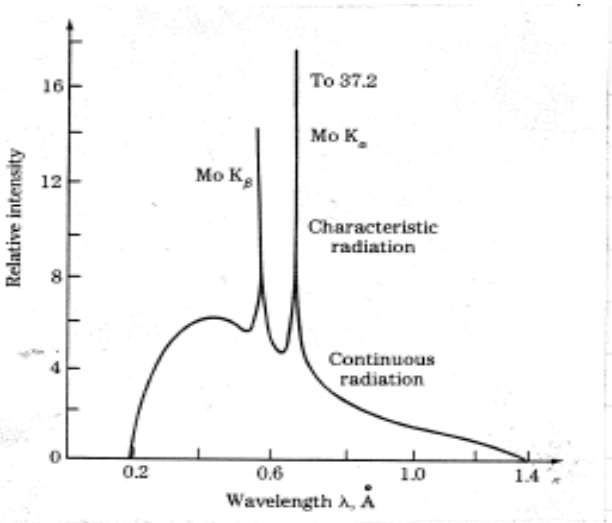


Crystal structure Analysis

用x-ray 探測結晶體的結晶構造

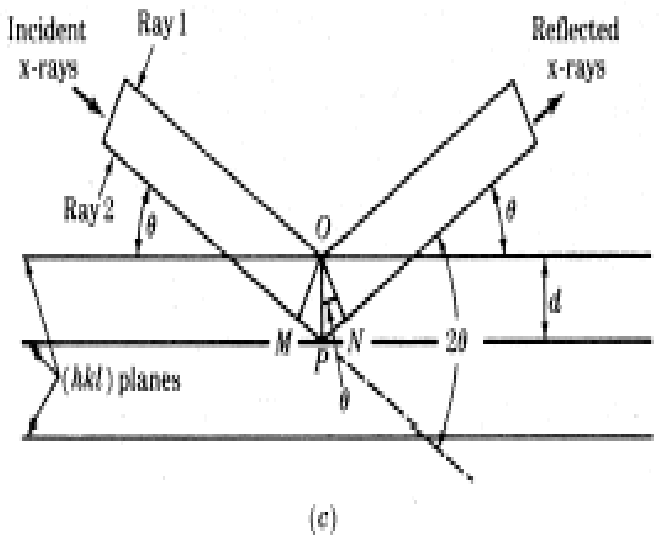
x-ray source

x-ray source微波長0.05~0.25 nm之電磁波各種不同的重元素被電子束撞擊激發出之x-ray波長亦不同. 如Mo之Kα, Kβ



x-ray diffraction

某些x光的波長大小和結晶固體的結晶面間距離大約相等，會生成繞射。



$n\lambda = Mp + pN$

n=1,2,3,. . . . . the order of the diffraction

由圖 $Mp = pN = d_{hkl} \sin\theta$

$\therefore n\lambda = 2d \sin\theta$

Bragg's Law

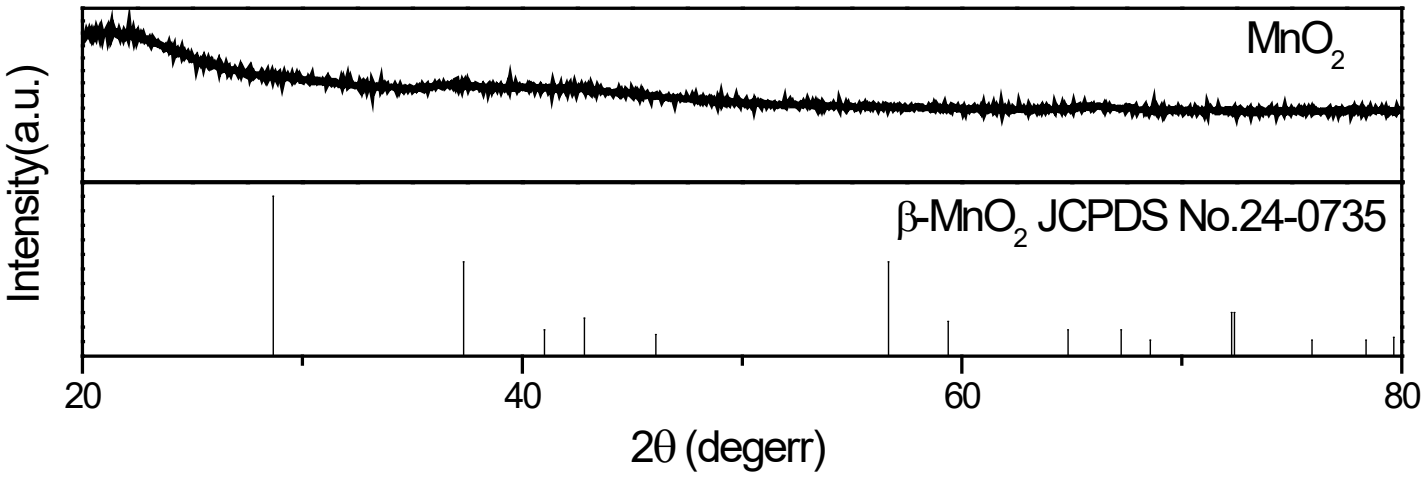
在大部分的情形下 n=1,即入 $= 2d_{hkl} \sin\theta$

X-Ray Diffraction Analysis (XRD) for Materials

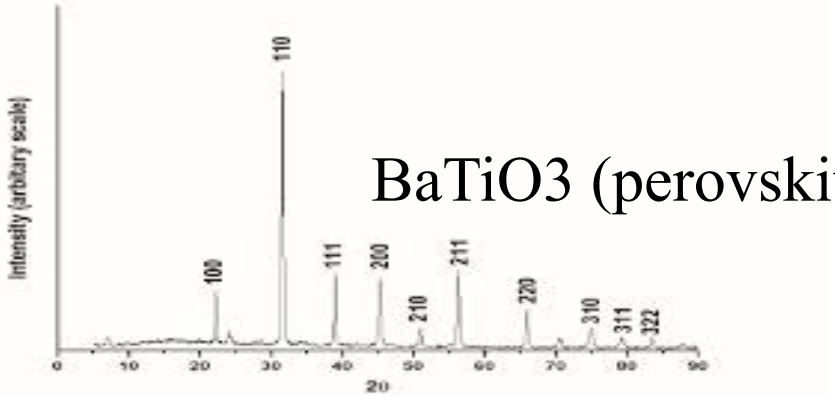
1. Crystal Examination:

Amorphous, polycrystal, single crystal

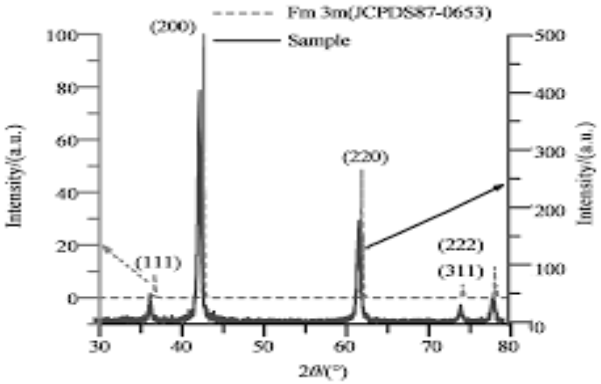
(a) **Amorphous**



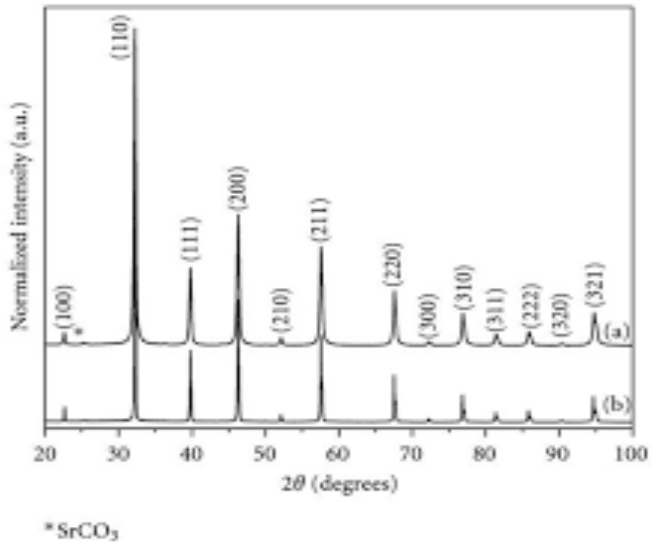
The as-prepared material is **an amorphous**.



BaTiO3 (perovskite)

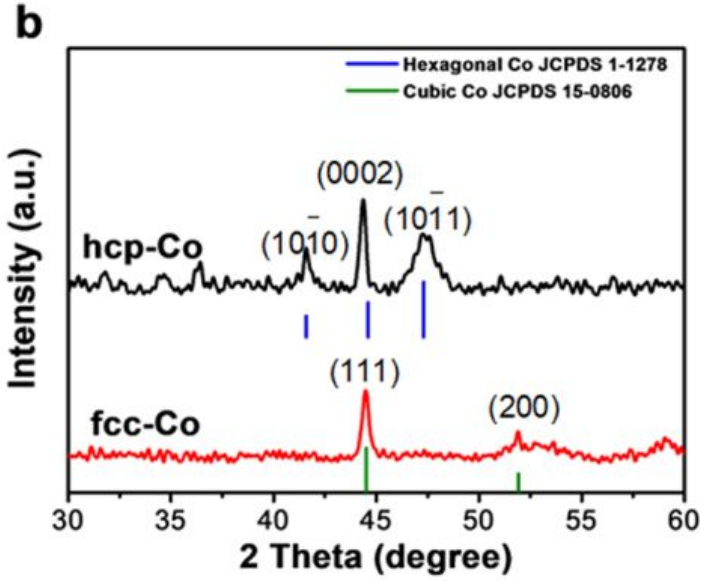


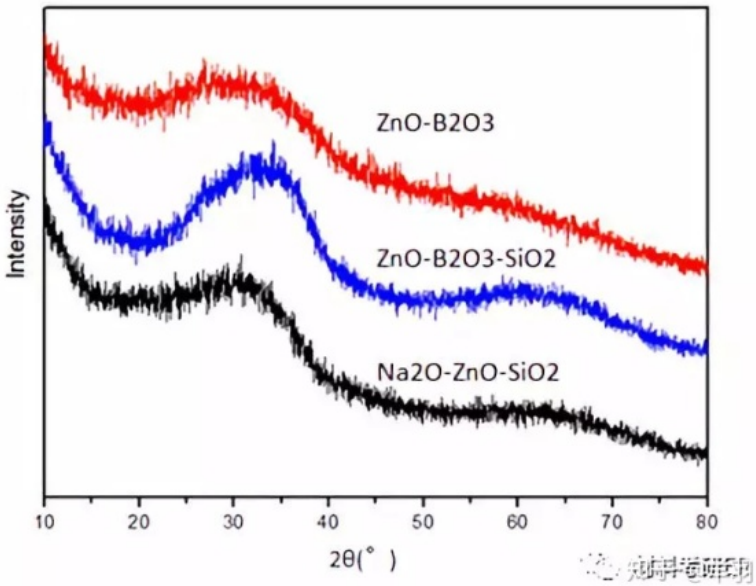
MgO

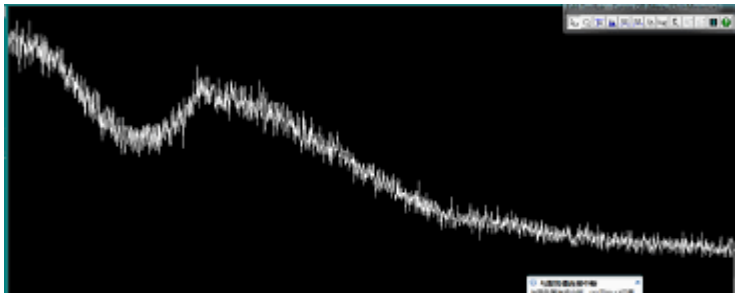


*$SrCO_3$

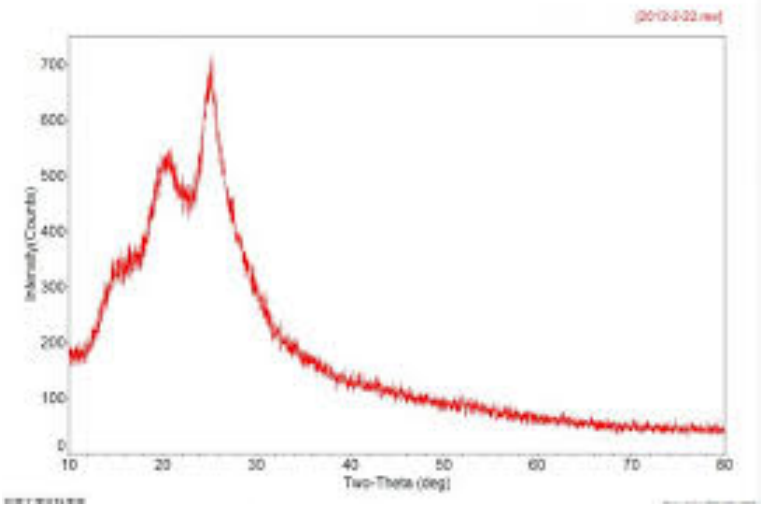
SrTiO3 (perovskite)



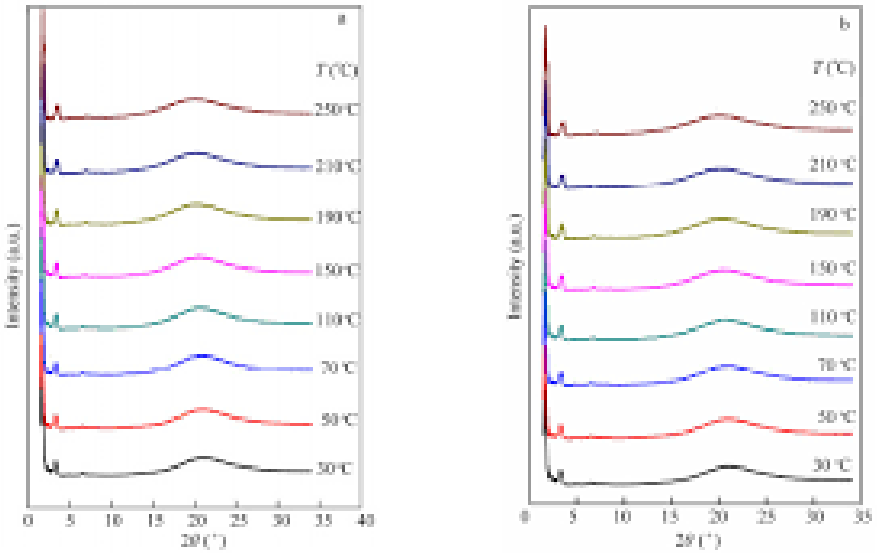




PVA



Polyamine



Polymerized Ionic **Liquid Crystals** with Different Alkyl Tail Length