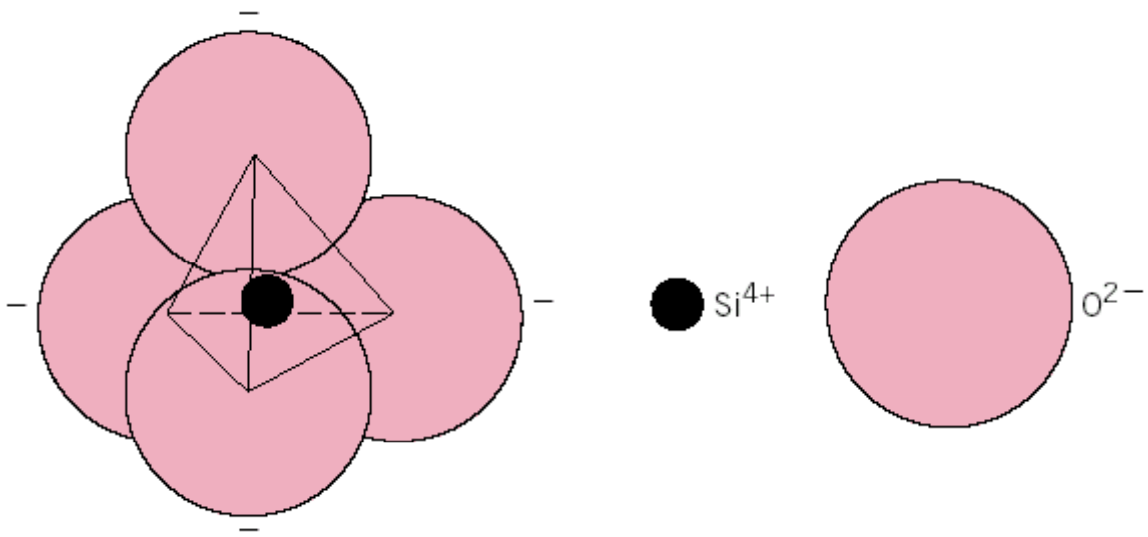
Silicate Ceramics

- Silicate : Si + O + 기타 원소
- Structure : SiO_4^{4-} tetrahedron is easier than unit cell
- Si-O 결합 : 공유결합성 (49%) → 방향성, 결합에너지 ↑

Table 3.2 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

Material	*Percent Ionic Character*
CaF_2	89
MgO	73
NaCl	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12



SiO_4^{4-} tetrahedron(사면체)

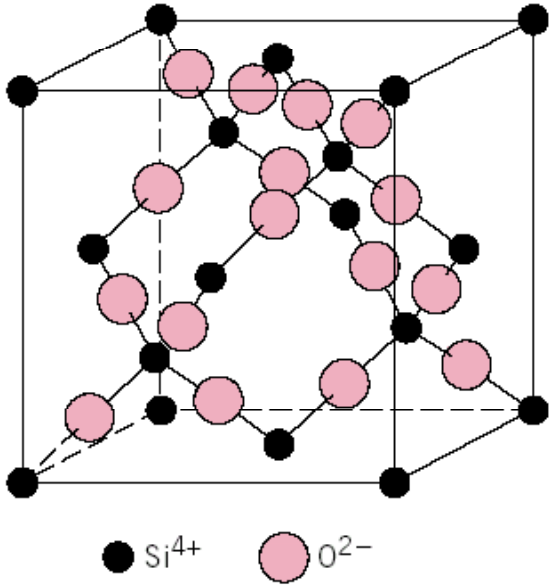
Crystal Structure of SiO_2

- SiO_2 : silicon dioxide or silica

for SiO_2

Si^{4+} : 0.041 nm
O^{2-} : 0.140 nm

$$\frac{r_{Si^{4+}}}{r_{O^{2-}}} = 0.293$$ ⇒ 가능한 배위수 비
→ 4:2, 2:1



※ 배위수를 최대로 하려는 경향 있슴
⇒ ∵ 이온주위에 반대 전하의 이온을 효율적으로 배치 가능

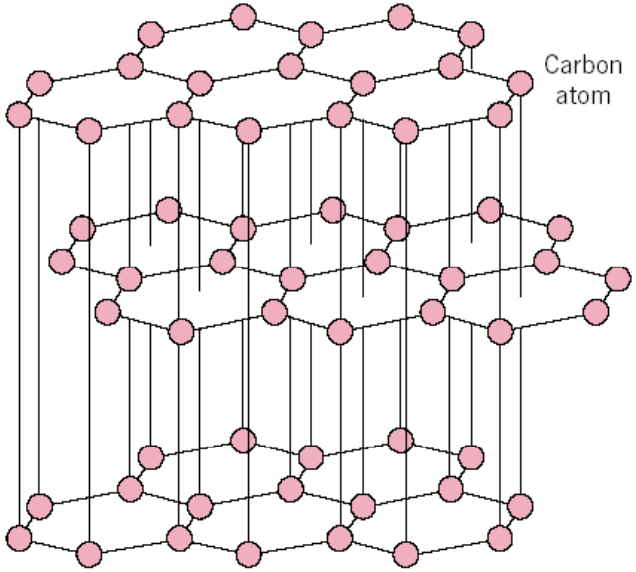
∴ 가장 안정한 4:2 배위를 가짐
⇒ Si^{4+} 이온 주위에 4개의 O^{2-} 이온 배치
⇒ O^{2-} 이온 주위에 2개의 Si^{4+} 이온 배치
⇒ 크리스토발라이트 (cristobalite)구조

Carbon

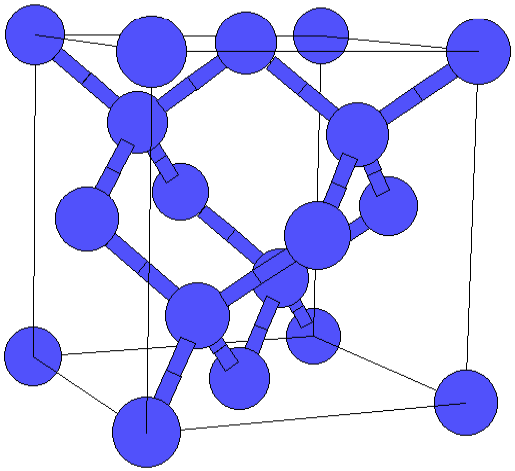
→ 같은 탄소 원소로만 이루어져 있으나 상(결정구조)이 다른 단체

- 흑연 (graphite)
- 다이아몬드 (diamond)
- 플러렌 (fullerene)

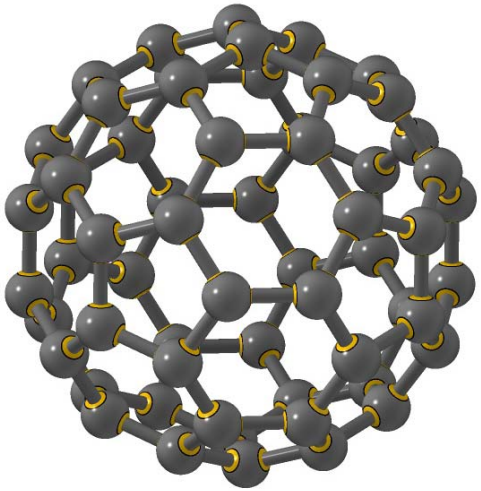
Polymorphism (Allotropy)



흑연



다이아몬드



플러렌

Graphite

원자좌표 : $000,\ \ 00\frac{1}{2},\ \frac{1}{3}\frac{2}{3}0,\ \frac{2}{3}\frac{1}{3}\frac{1}{2}$

(0001)면 적층 → ABABAB or ACACAC

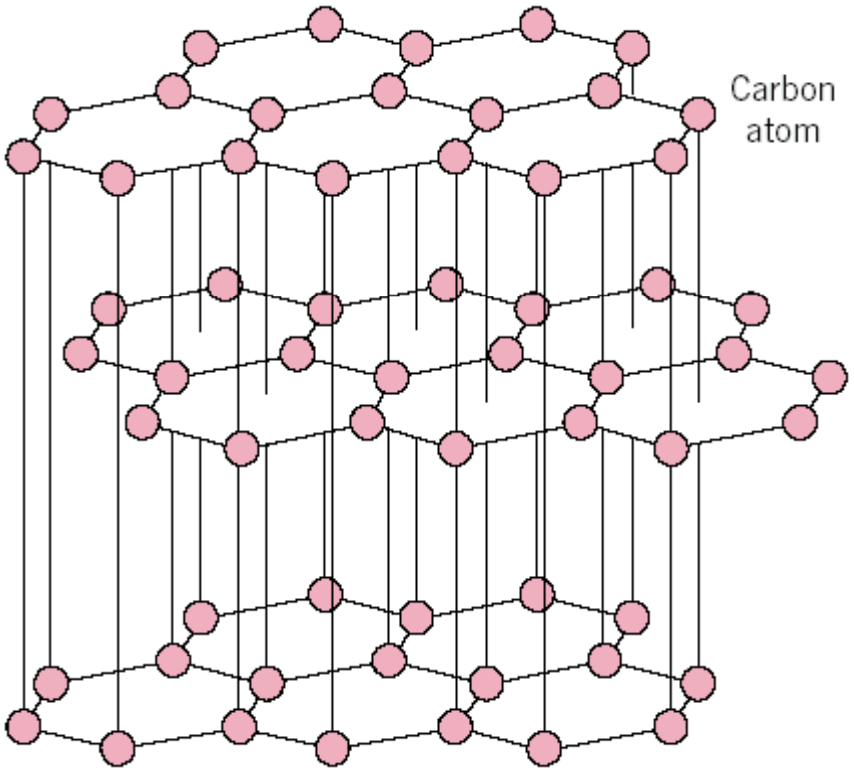
배위수 = 3개

최인접원자까지의 거리 $= \frac{1}{\sqrt{3}}a$

→ 0.142 nm

층간거리 $= 0.335\text{nm}$ → $C = 2\times$ 층간거리

→층상구조(윤활제)



Diamond

원자좌표 : $000, \ \frac{1}{4}\frac{1}{4}\frac{1}{4}$

최인접원자까지의 거리 $= \frac{\sqrt{3}}{4}a$

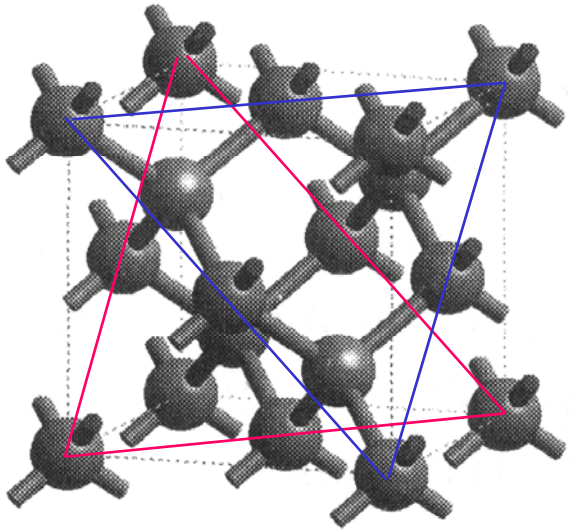
정사면체 → 배위수 = 4

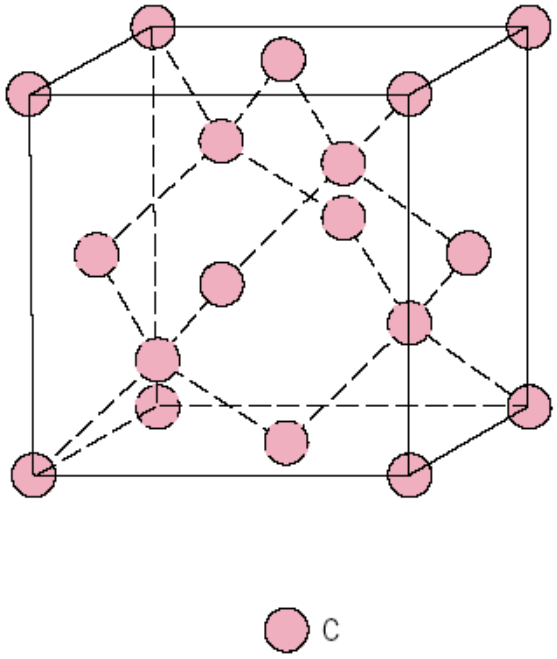
(111)면 적층 → CAABBCCAABBC

$$\text{APF} = \frac{\sqrt{3}\pi}{16} = 0.34$$ (bcc의 반)

면심입방의 다이아몬드 영진
→ 면심입방의 1/41/41/4 변위 구조

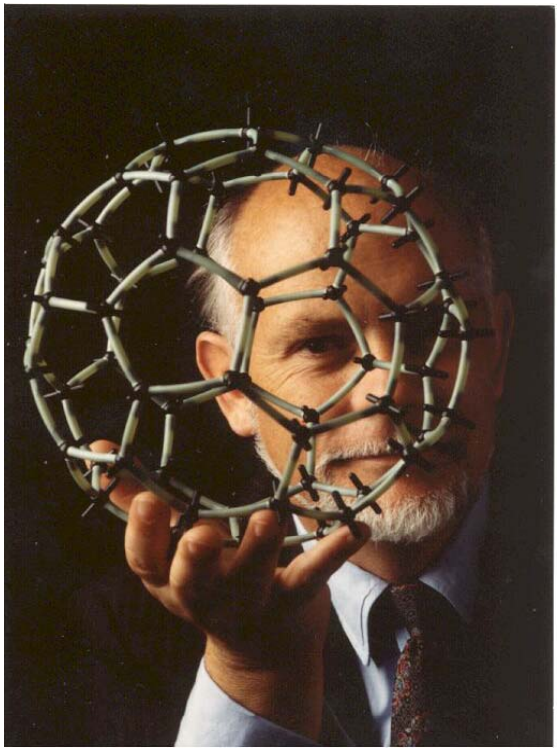
(예) Si, Ge, Sn...

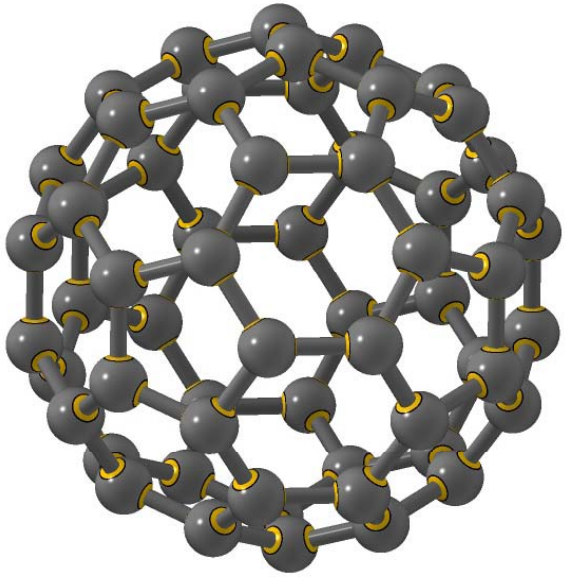


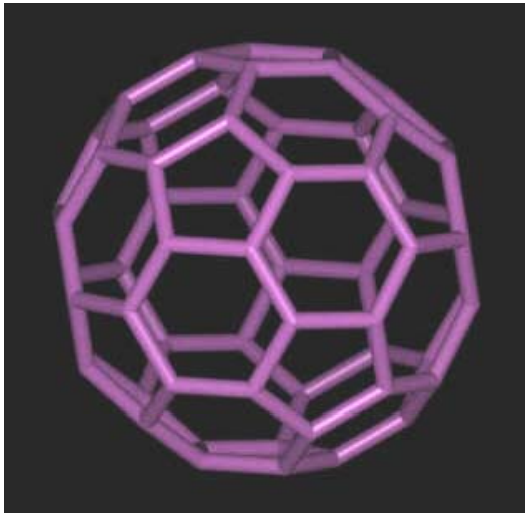


Fullerenes

- C_{60} (탄소원자 60개로 이루어진 구조)
- 1985년 Richard E. Smalley 발견
- 미국 건축가 Buckminster Fuller가 창안한 geodesic dome과 유사하여 이름을 따옴
  → "Buckminsterfullerene"
  → "Buckyball" 또는 "Fullerene"



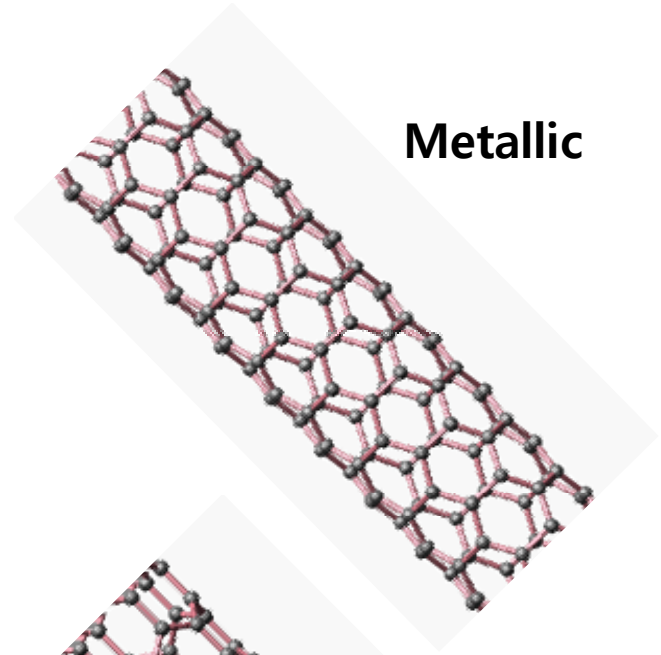




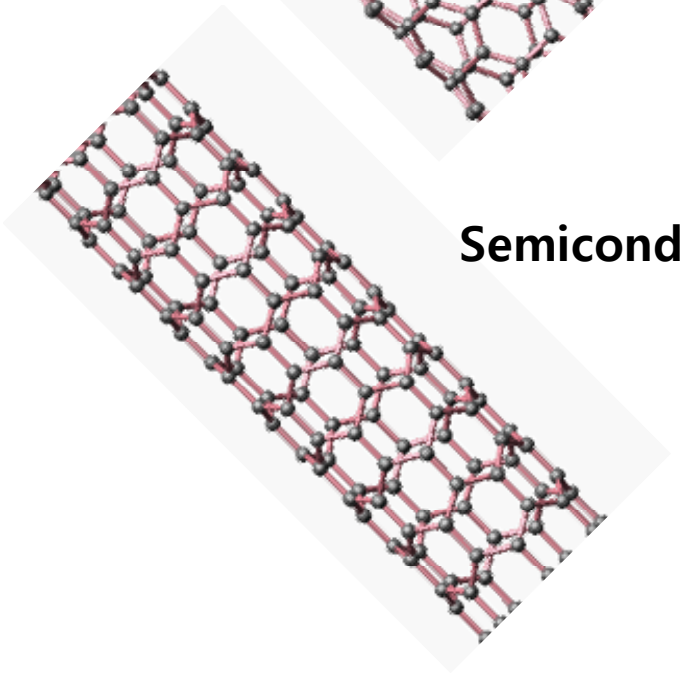
Nanotube

- Electrical Properties

- Mechanical Properties:



Metallic



Semiconducting

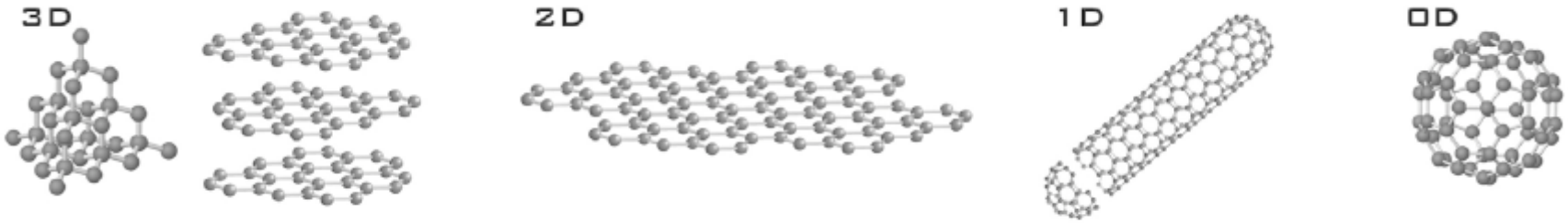


Fig. 1 Crystal structures of the different allotropes of carbon. (Left to right) Three-dimensional diamond and graphite (3D); two-dimensional graphene (2D); one-dimensional nanotubes (1D); and zero-dimensional buckyballs (0D). (Adapted and reprinted with permission from[66]. © 2002 Prentice Hall.)

crystal system

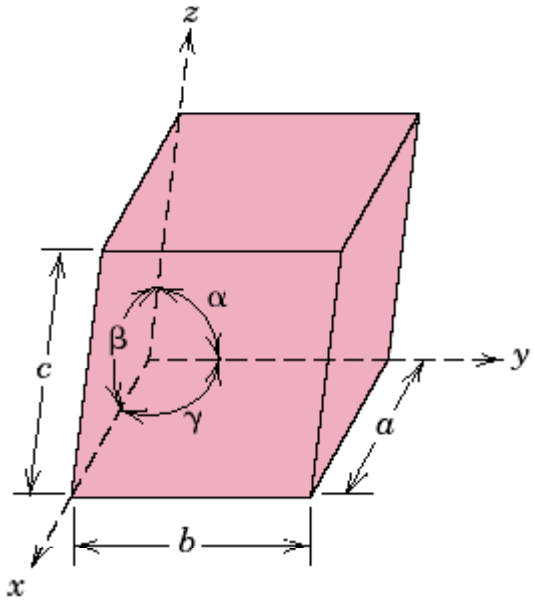
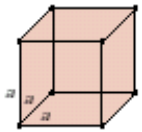
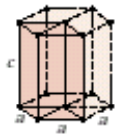
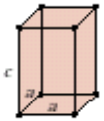
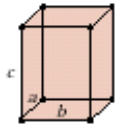
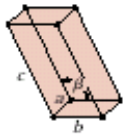
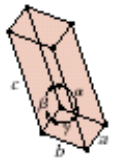


Table 3.6 Lattice Parameter Relationships and Figures Showing Unit Cell Geometries for the Seven Crystal Systems

Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	

Crystal Lattice Structures - Microsoft Internet Explorer

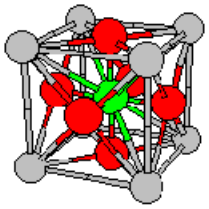
파일(F) 편집(E) 보기(V) 즐겨찾기(A) 도구(T) 도움말(H)

주소(D) http://cst-www.nrl.navy.mil/lattice/index.html

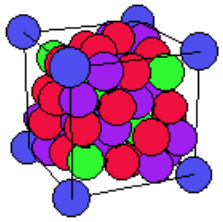
Crystal Home | Strukturbericht Index | Pearson Symbol | Space Group | Prototype Index | FAQ | References | Other Sites | NRL Home | M&TD Home | CCM&S Home | No Frames

Additions to the database? Read this first.

Questions? See the FAQ



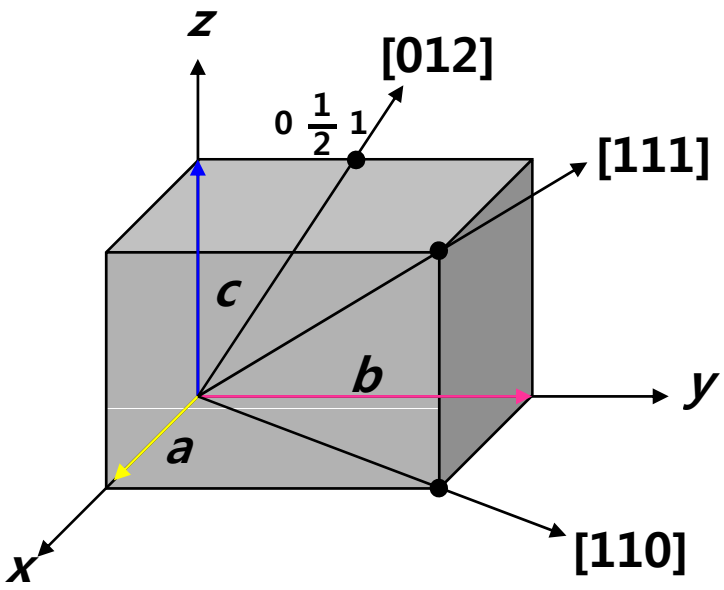
Crystal Lattice* Structures

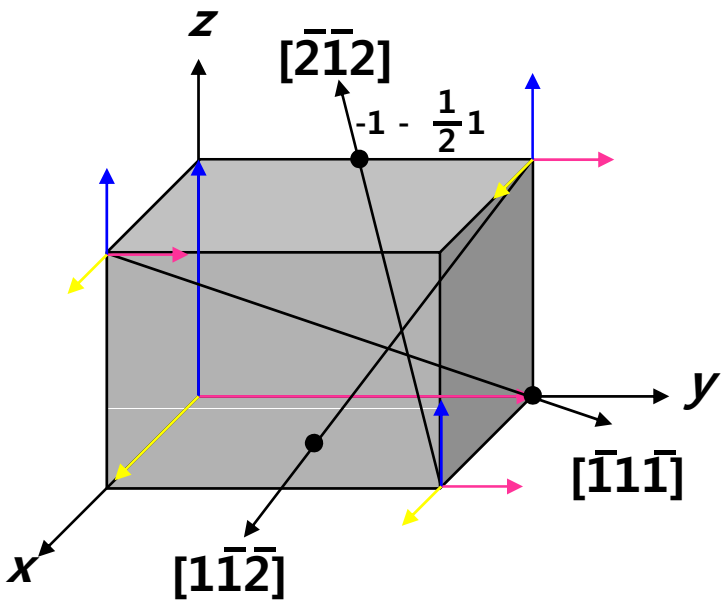


Indexed by	
Strukturbericht Designation	Pearson Symbol
Space Group	Prototype

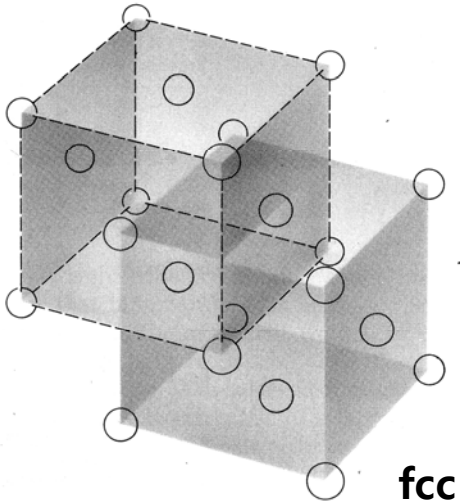
The Crystal Structure of Intermetallic Alloy Phases

Crystallographic Directions

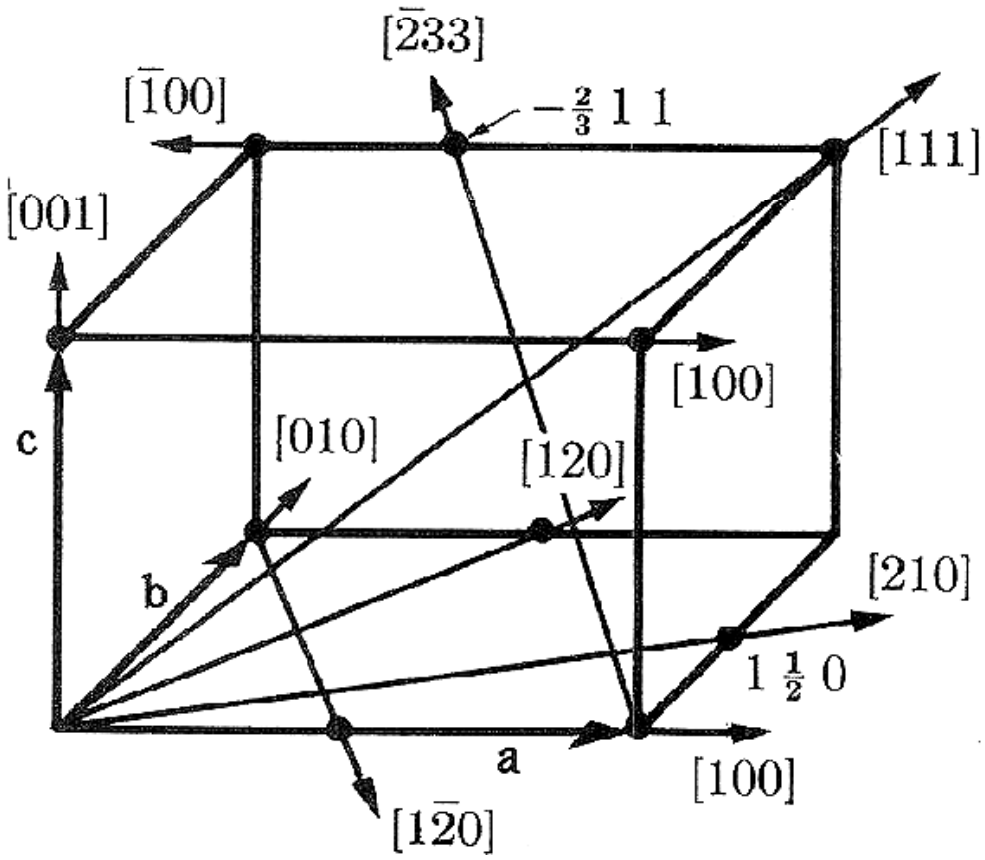


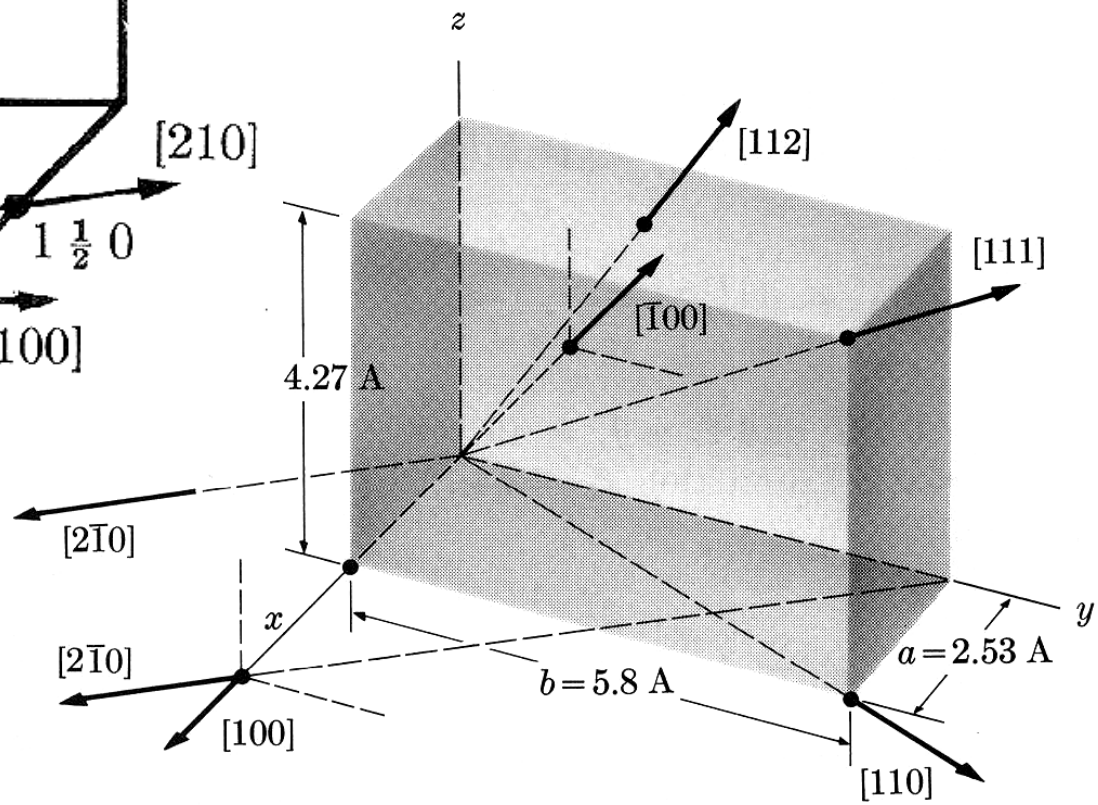


※모든 격자점은 동등한 주위 환경을 가지므로
모두 원점이 될 수 있다.
→ 기준축의 설정이 관건



fcc 결정


[$\bar{2}$33]
[$\bar{1}$00]
$-\frac{2}{3}$ 1 1
[111]
[001]
[100]
c
[010]
[120]
b
[210]
1 $\frac{1}{2}$ 0
a
[100]
[1$\bar{2}$0]

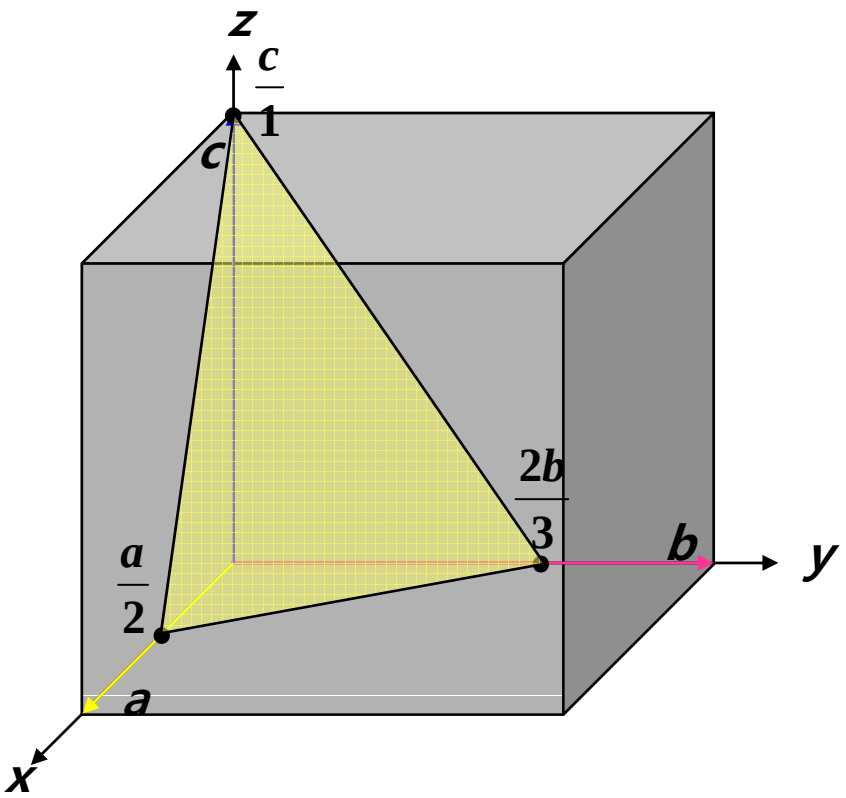

z
[112]
[111]
[$\bar{1}$00]
4.27 A
[2$\bar{1}$0]
x
y
[2$\bar{1}$0]
$a = 2.53$ A
$b = 5.8$ A
[100]
[110]

Crystallographic Plane

→ [hkl] 방향에 수직인 면 또는 세 축과의 교차 형태로 표현

→ 임의의 격자면이 원점에서 각각거리 a/h, b/k, c/l 만큼 떨어져 세 축과 만날 때 이 격자면을 (h k l)면이라 함. h, k, l 은 정수

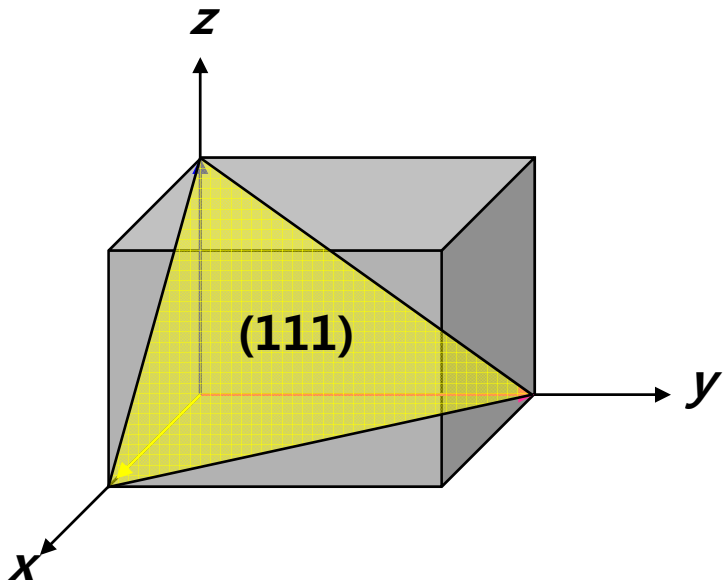
→ 축과의 교점까지의 거리비의 역수를 간단한 정수비로 표현

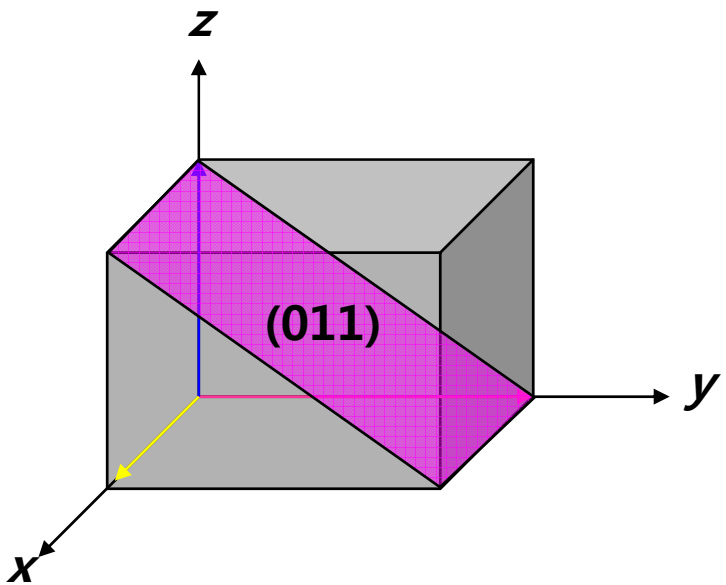


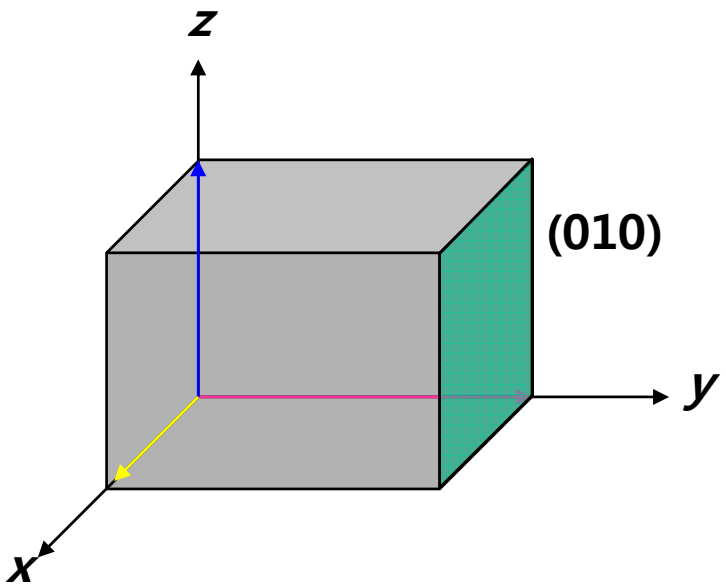
	x	y	z
→	$\frac{a}{2}$	$\frac{2b}{3}$	$\frac{c}{1}$
→	$\frac{a}{4}$	$\frac{b}{3}$	$\frac{c}{2}$

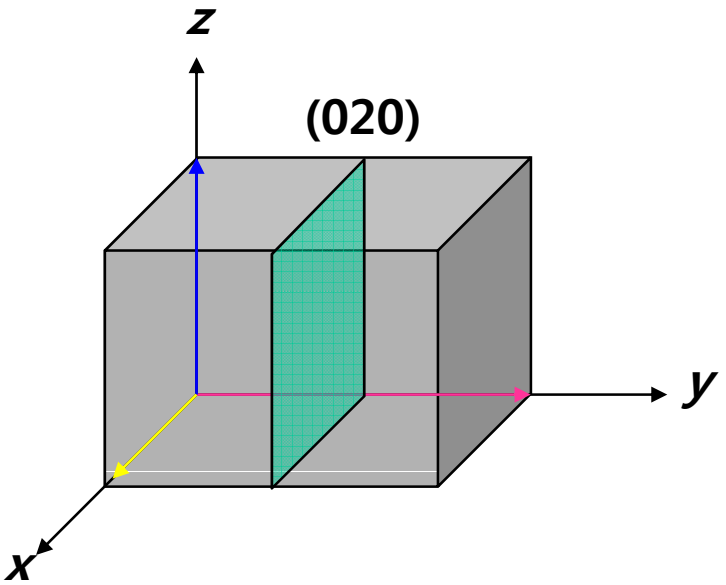
⇒ (4 3 2) 면

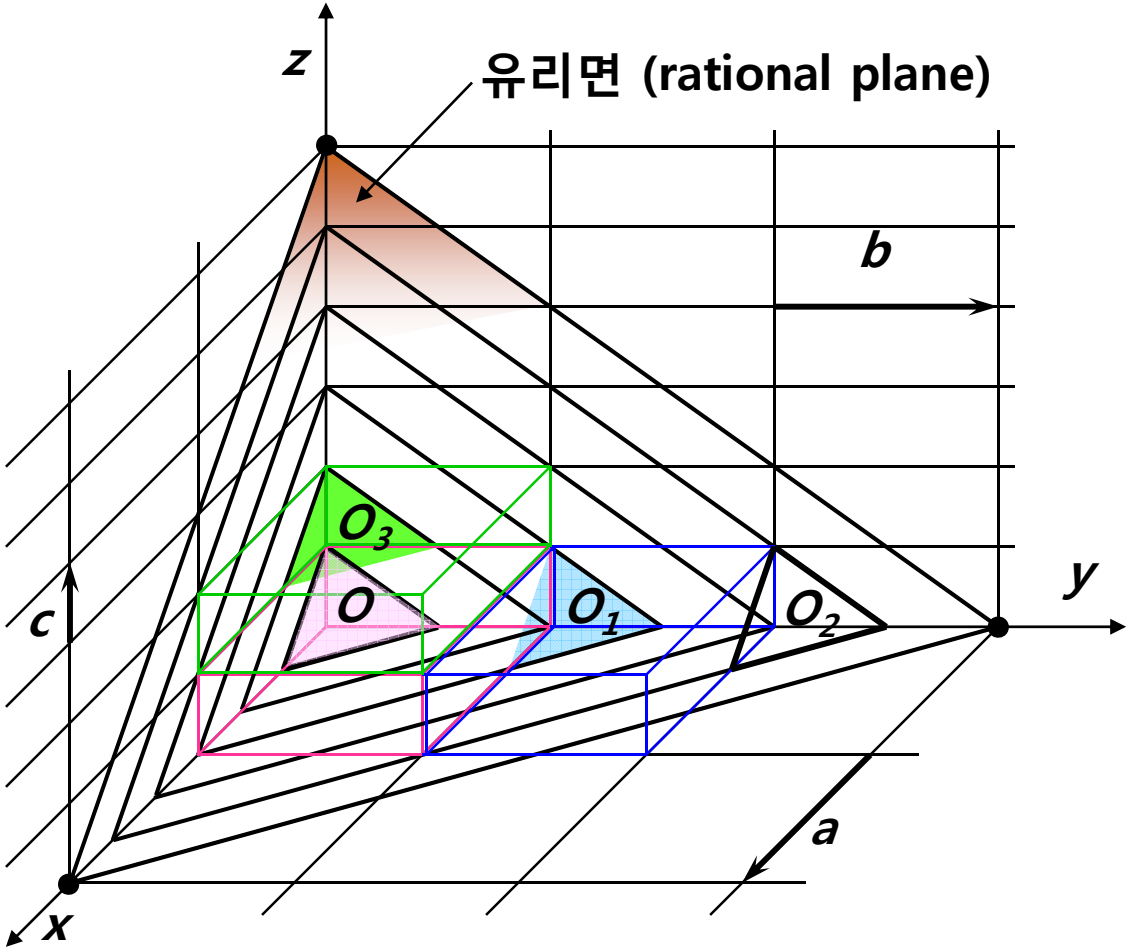
※ 축과 만나지 않는 경우
→ 거리(∞)비의 역수 = 0
→ (h k 0), (h 0 0) 등과 같이 표현


z
y
x
(111)


z
y
x
(011)


z
y
x
(010)

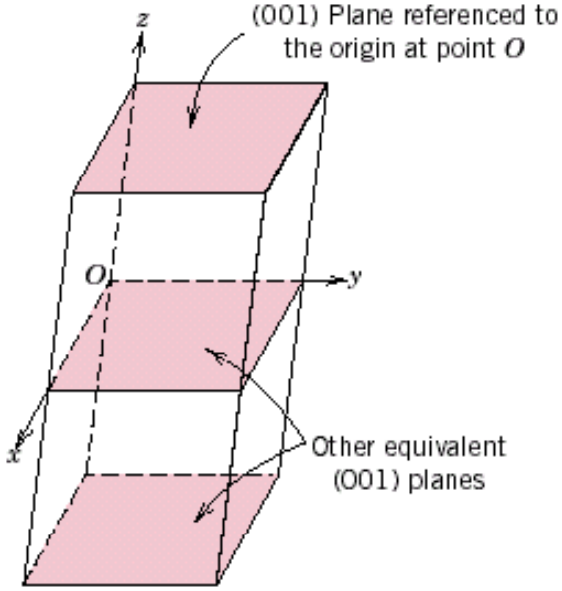

z
(020)
y
x

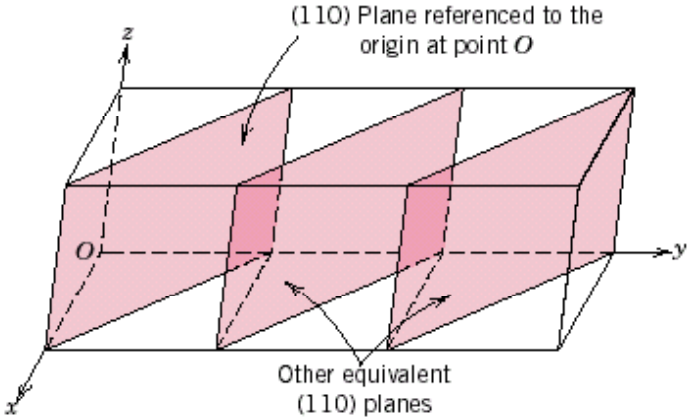


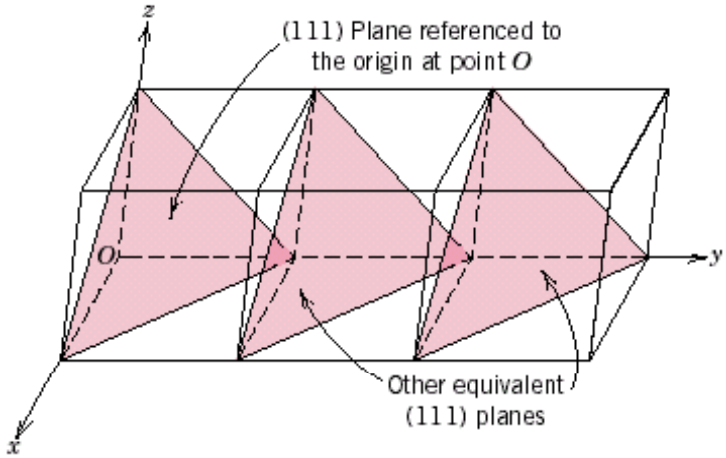
격자면 (321)

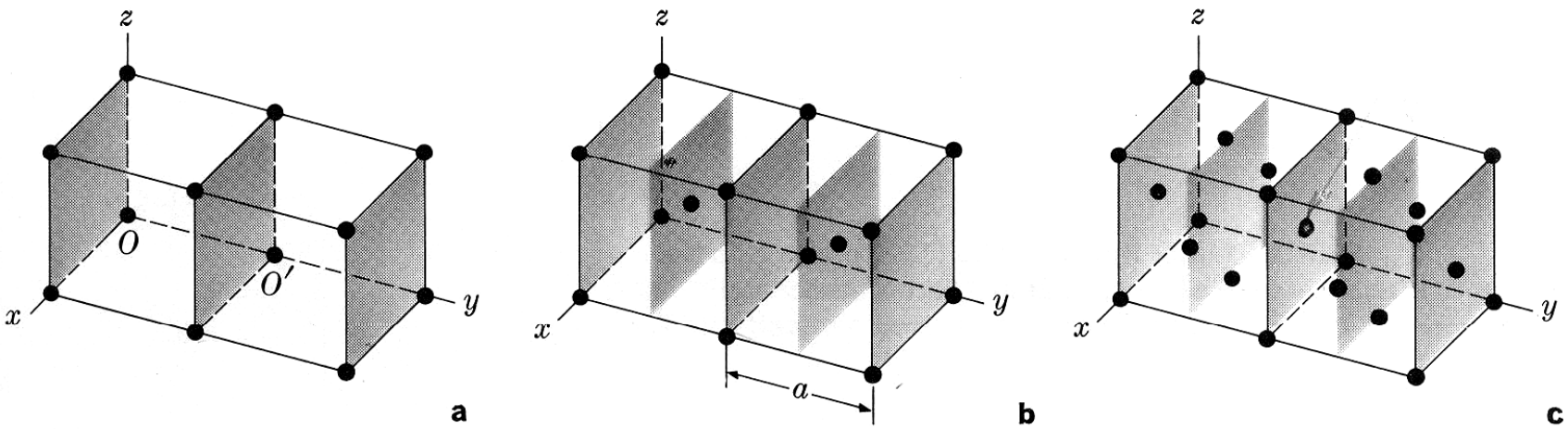
equivalent plane

※모든 격자점은 동등한 주위 환경을 가지므로 모두 원점이 될 수 있다.
→ 기준축의 설정이 관건

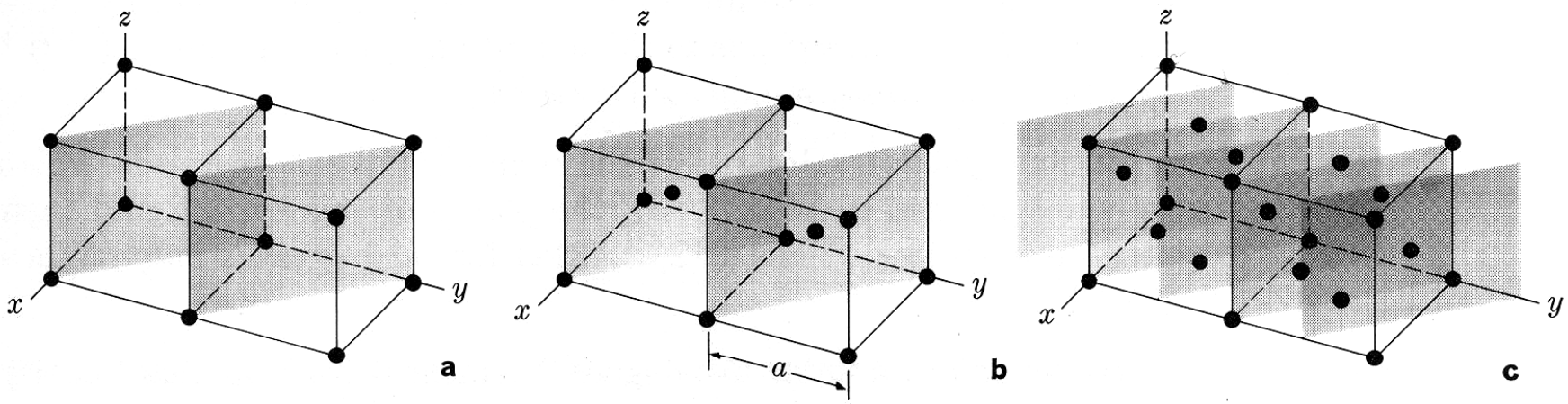




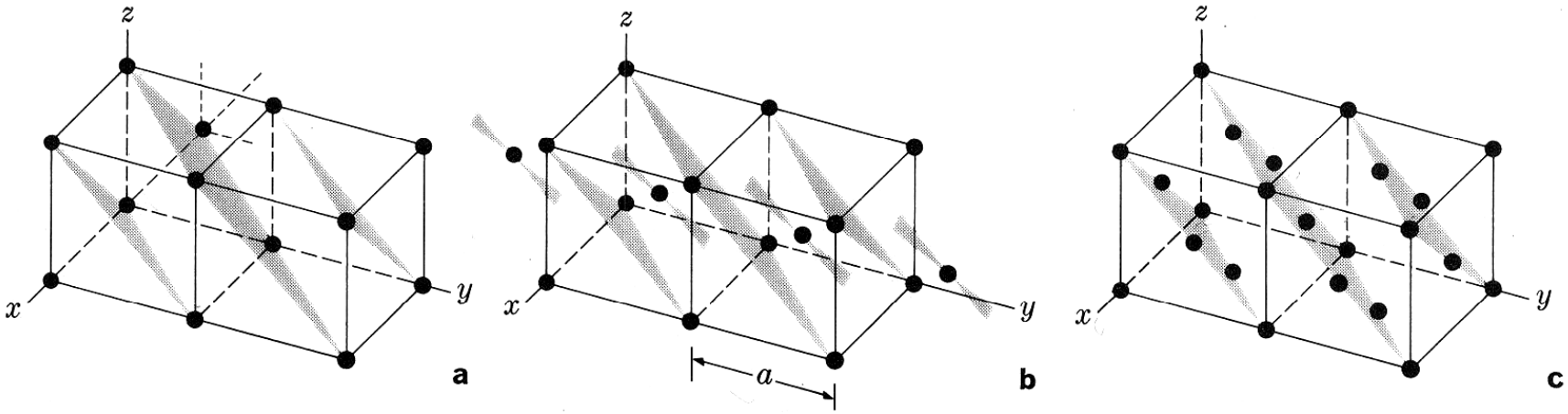




5-13 (010) planes in cubic structures. (a) Simple cubic. (b) bcc. (c) fcc. [Note that the 020 planes included for bcc and fcc are equivalent to (010) planes.]



5-14 (110) planes in cubic structures. (a) Simple cubic. (b) bcc. (c) fcc. [The 220 planes included for fcc are equivalent to (110) planes.]



5-15 $(\bar{1}11)$ planes in cubic structures. (a) Simple cubic. (b) bcc. (c) fcc. Negative intercepts are indicated by bars above the index. [The $\bar{2}22$ planes included for bcc are equivalent to $(\bar{1}11)$ planes.]

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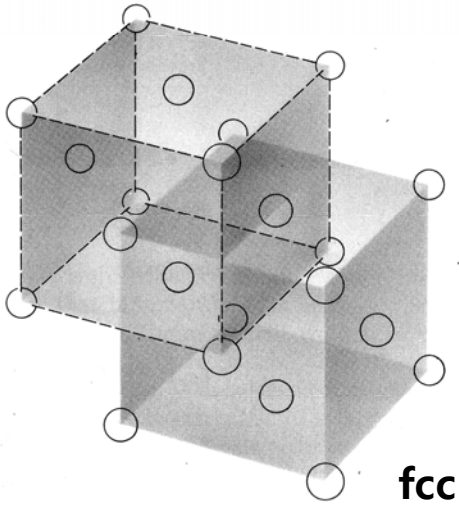
모두 원점이 될 수 있다.
→ 기준축의 설정이 관건



fcc 결정

※ 격자면 (lattice plane) vs. 결정면 (crystal plane)

- 격자면 : (h k l) ≠ (nh nk nl) → ∵ 면간격이 다름
- 결정면 : h, k, l 이 공약수를 갖지 않도록 표현 → 평행한 면들의 대표

  (h k l) = (nh nk nl)

※ 면족 (group, family) or 면형 (form)

⇒ { h k l } 로 표시

예) 단순 입방정 {100} → 6개 동가면 (∵ 4개의 3회 회전대칭에 의해)

(100), (010), (001)

$(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$

단순 정방정 {100} → 4개 동가면 (∵ 4회 회전대칭에 의해)

(100), (010), $(\bar{1}00)$, $(0\bar{1}0)$

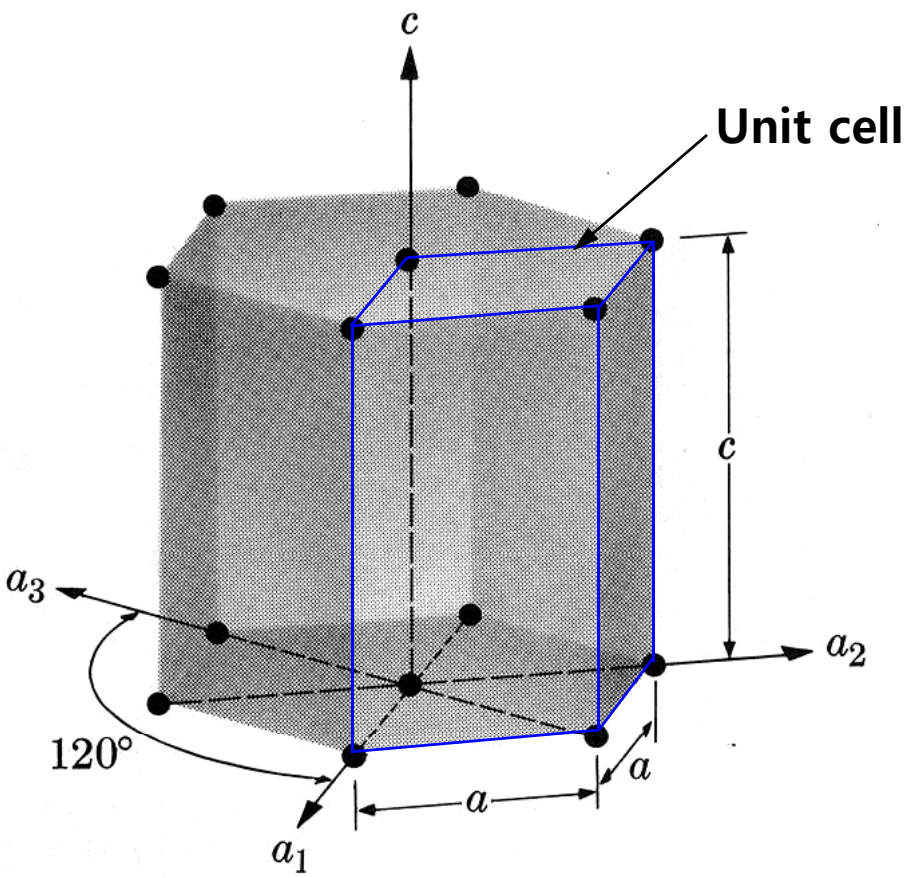
≠

{001} → 2개 동가면 (∵ 2회 회전대칭에 의해)

(001), $(00\bar{1})$

⇒ 다중도 (multiplicity) : 면족에 속하는 격자면의 수

hcp

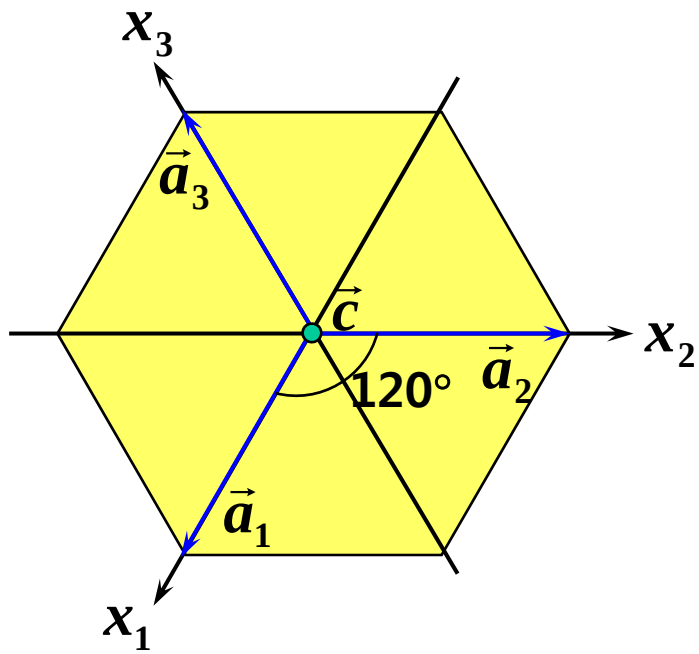


$a_1 = a_2 \neq c$

$a = b = 90° \neq g = 120°$

4축 좌표계로 표현

$a_1 = a_2 = a_3 \neq c$



⇒ Miller-Bravais 지수 (4개의 지수) 이용

- 격자방향 (lattice direction)

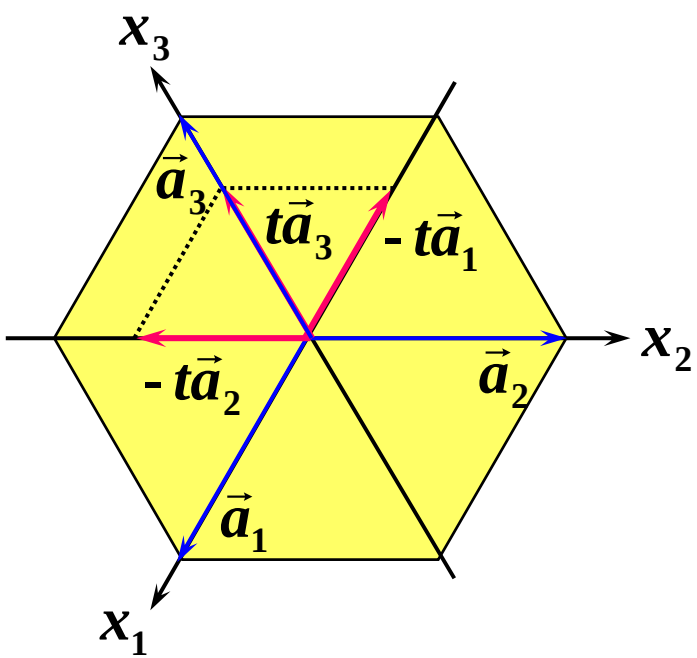
3축 좌표계 → [*U V W*]

4축 좌표계 → [*u v t w*]

$$U = u - t \qquad u = \frac{1}{3}(2U - V)$$

$$V = v - t \qquad v = \frac{1}{3}(2V - U)$$

$$W = w \qquad t = -(u+v) = -\frac{1}{3}(U+V)$$



$$|\vec{a}_1| = |\vec{a}_2| = |\vec{a}_3|$$

2차원 상에서

3축 좌표계 : $\vec{r} = U\vec{a}_1 + V\vec{a}_2$

4축 좌표계 : $\vec{r} = u\vec{a}_1 + v\vec{a}_2 + t\vec{a}_3$

⇒ $t\vec{a}_3$ 를 x_1 방향과 x_2 방향으로 분해

$$t\vec{a}_3 = -(t\vec{a}_1 + t\vec{a}_2)$$

$$\therefore \quad \vec{r} = u\vec{a}_1 + v\vec{a}_2 + t\vec{a}_3 = u\vec{a}_1 + v\vec{a}_2 - (t\vec{a}_1 + t\vec{a}_2)$$

$$= (u-t)\vec{a}_1 + (v-t)\vec{a}_2$$

$$\equiv U\vec{a}_1 + V\vec{a}_2$$

$$\Rightarrow \quad U = u - t, \quad V = v - t, \quad W = w$$

$$U + V = (u-t) + (v-t) = (u+v) - 2t$$

$$= -3t \qquad (\because \ t = -(u+v))$$

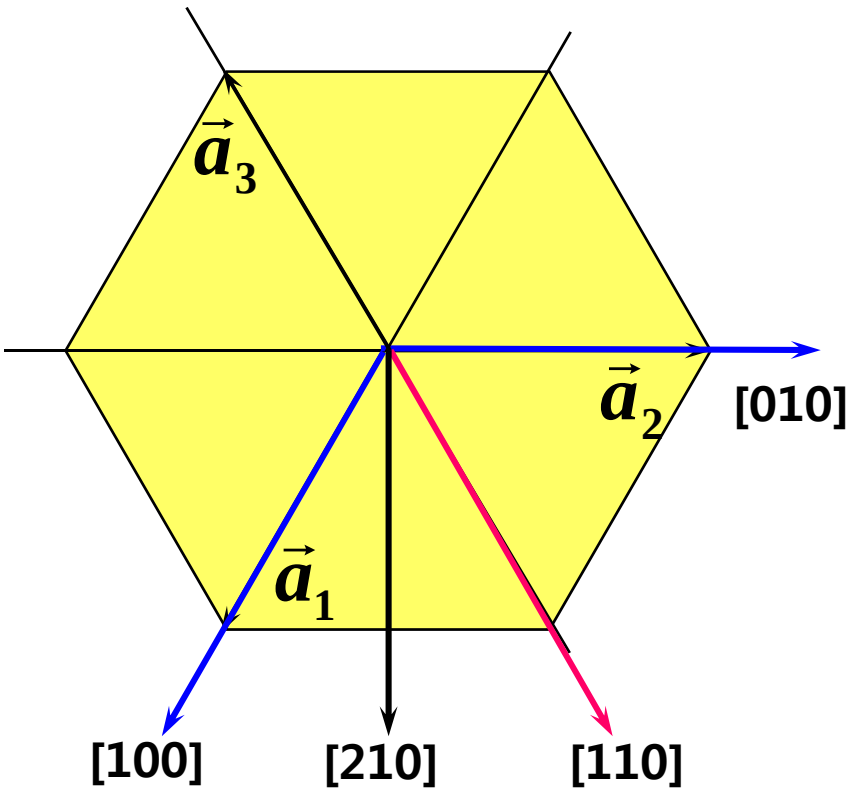
$$\therefore \ t = -\frac{1}{3}(U+V)$$

$$u = U + t = U - \frac{1}{3}(U+V) = \frac{1}{3}(2U - V)$$

$$v = V + t = V - \frac{1}{3}(U+V) = \frac{1}{3}(2V - U)$$

$$\Rightarrow \quad u = \frac{1}{3}(2U - V), \quad v = \frac{1}{3}(2V - U), \quad t = -(u+v) = -\frac{1}{3}(U+V)$$

※ 육방정계의 방향은 3축 좌표계 (Miller 지수)를 이용하는 것이 편리



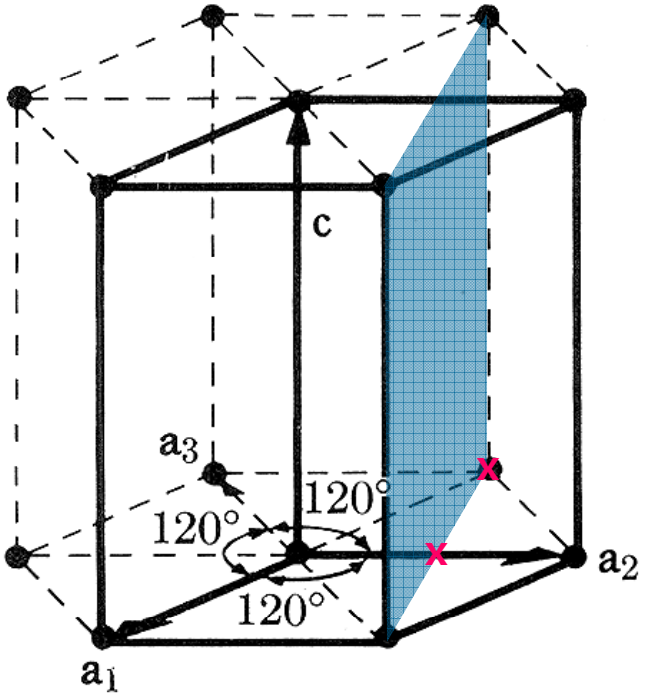
3축 좌표계	4축 좌표계
[100]	$[2\bar{1}\bar{1}0]$
[210]	$[10\bar{1}0]$
[110]	$[11\bar{2}0]$
[010]	$[\bar{1}2\bar{1}0]$

⇒ Miller-Bravais 지수 (4개의 지수) 이용

- 격자면 (lattice plane)

3축 좌표계 → (*h k l*)
4축 좌표계 → (*h k i l*)

$$h + k = -i$$



	a_1	a_2	c
거리비 →	-1	1/2	∞
역수비 →	-1	2	0

∴ h = -1, k = 2, l = 0

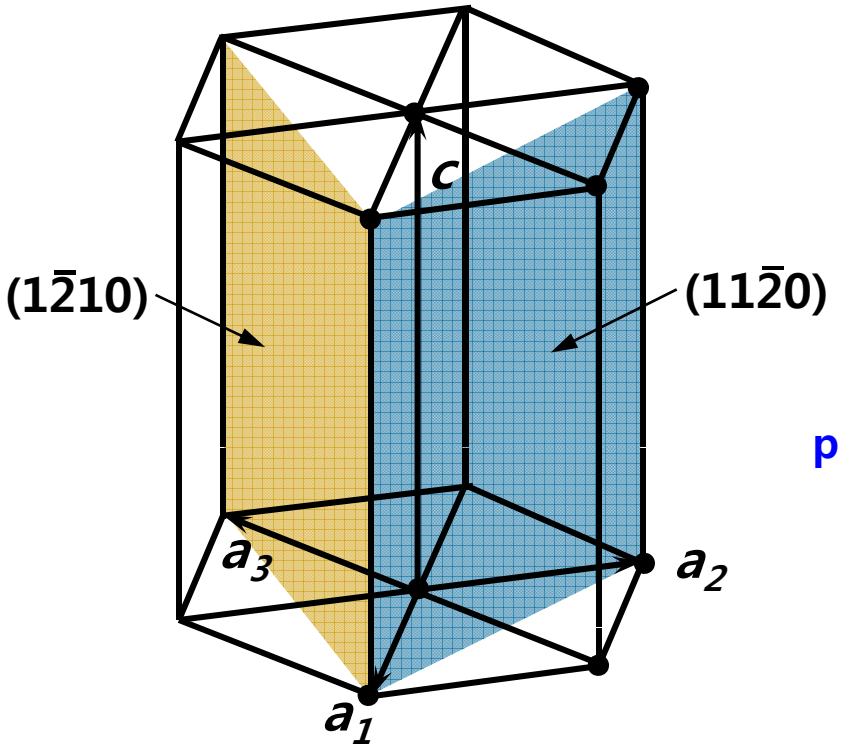
$h + k = 1 = -i$

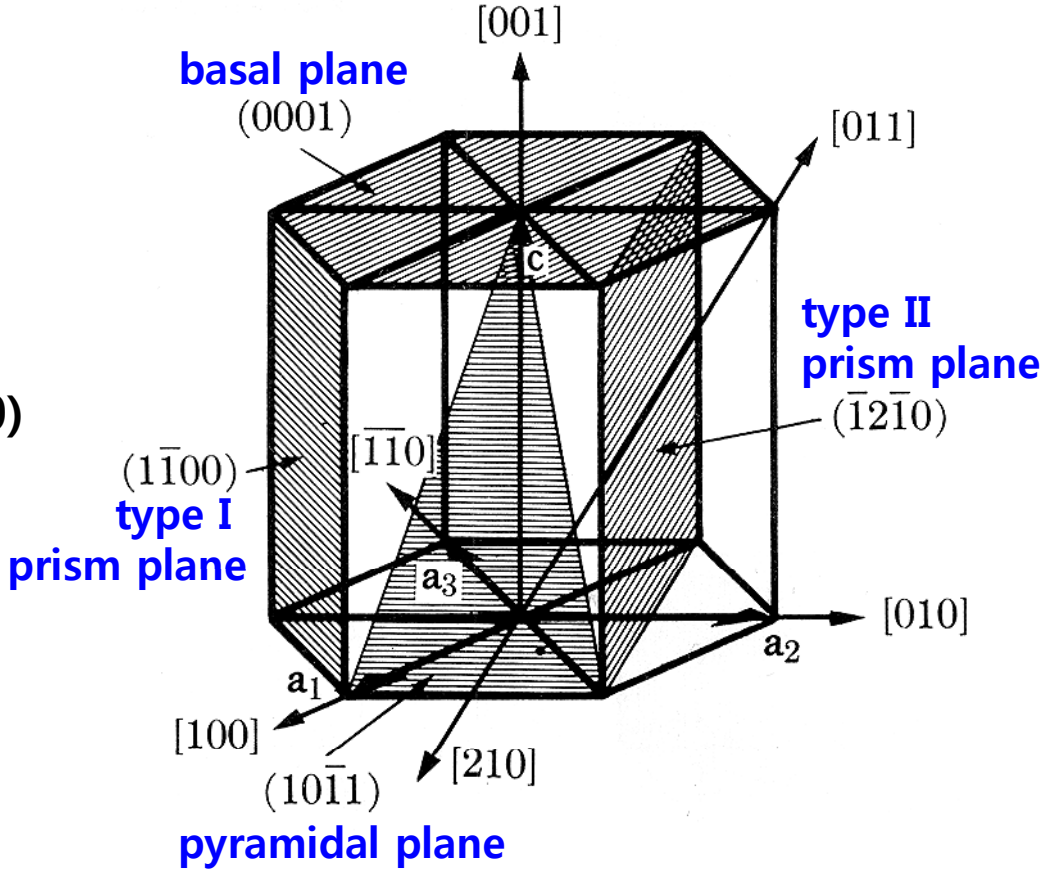
∴ i = -1

⇒ Miller-Bravais 지수 = $(\bar{1}2\bar{1}0)$

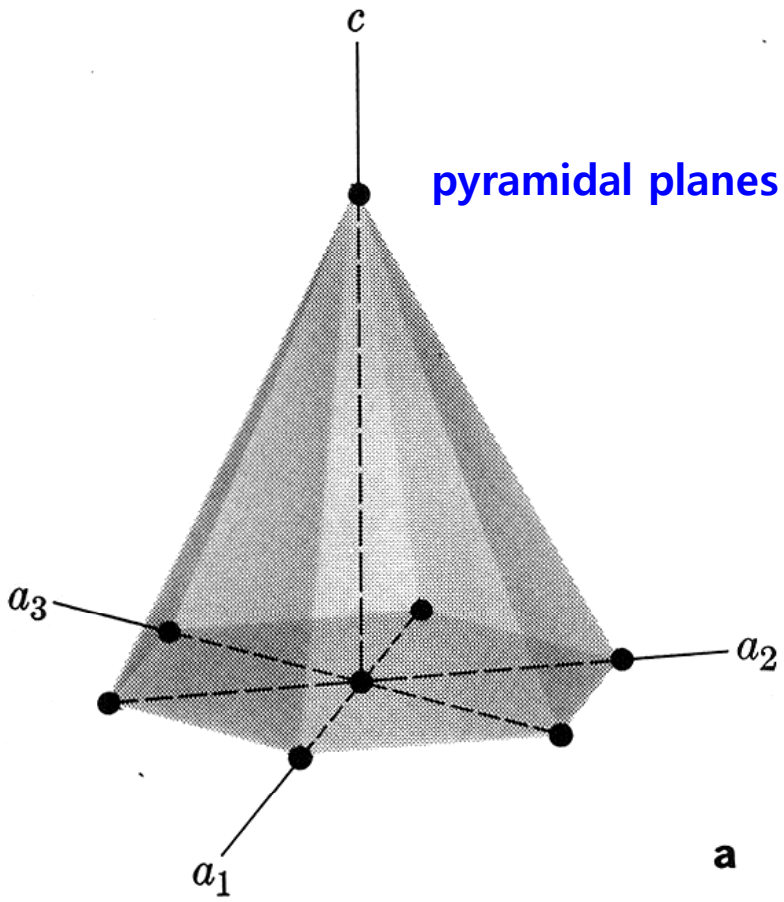
- 육방정계의 격자면은 Miller-Bravais 지수를 이용하는 것이 유리
  → 동가의 격자면 표현에 편리 예) $(11\bar{2}0)$, $(1\bar{2}10)$

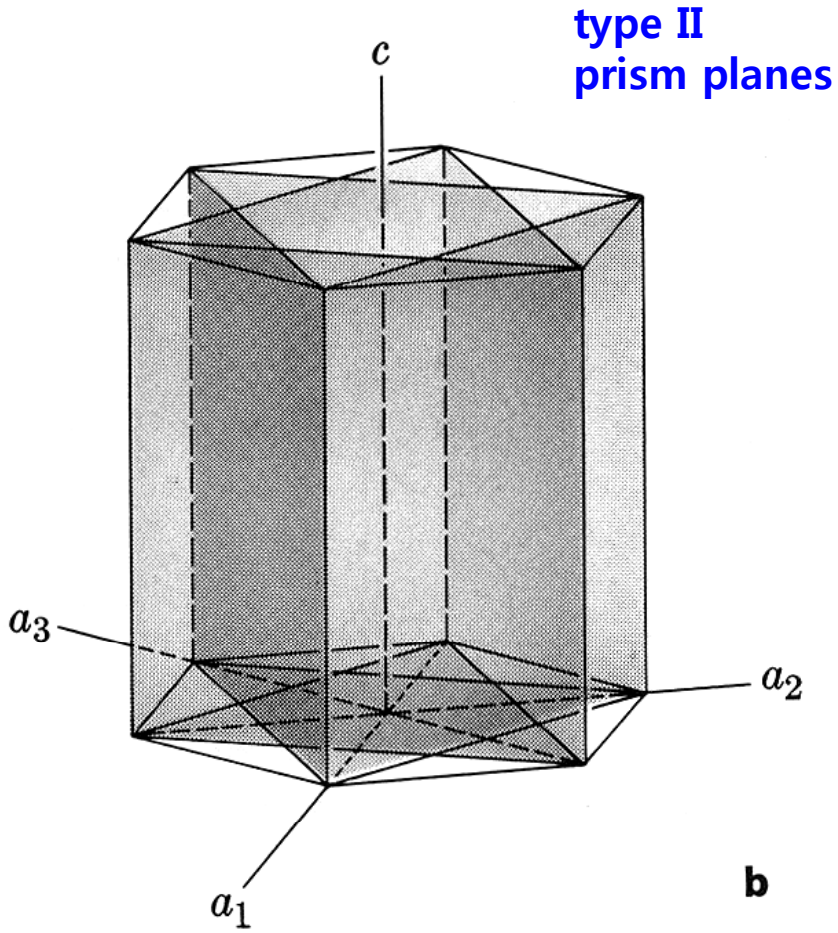
M-B	→	Miller
$(11\bar{2}0)$	→	(110)
$(1\bar{2}10)$	→	$(1\bar{2}0)$



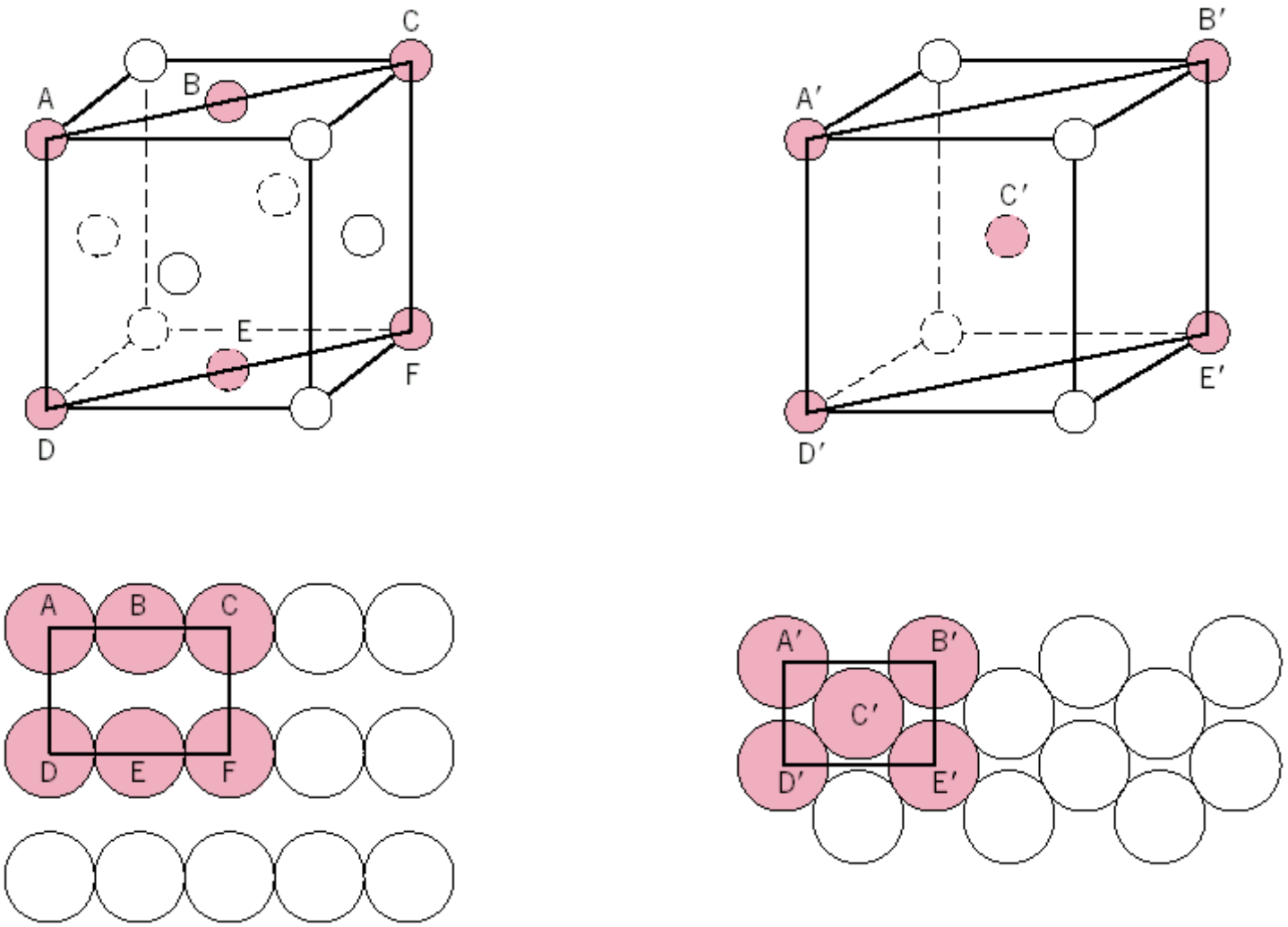


family/form





5-20 Miller-Bravais indices. (a) $\{10\bar{1}1\}$ form. This form also includes six more planes which produce an inverted hexagonal pyramid below the basal plane. (b) $\{11\bar{2}0\}$ form. The form includes $(11\bar{2}0)$, $(1\bar{2}10)$, $(\bar{2}110)$, $(\bar{1}\bar{1}20)$, $(\bar{1}2\bar{1}0)$, and $(2\bar{1}\bar{1}0)$ planes to complete a hexagonal prism. The unit cell is enclosed by $\{10\bar{1}0\}$ and $\{0001\}$ planes.



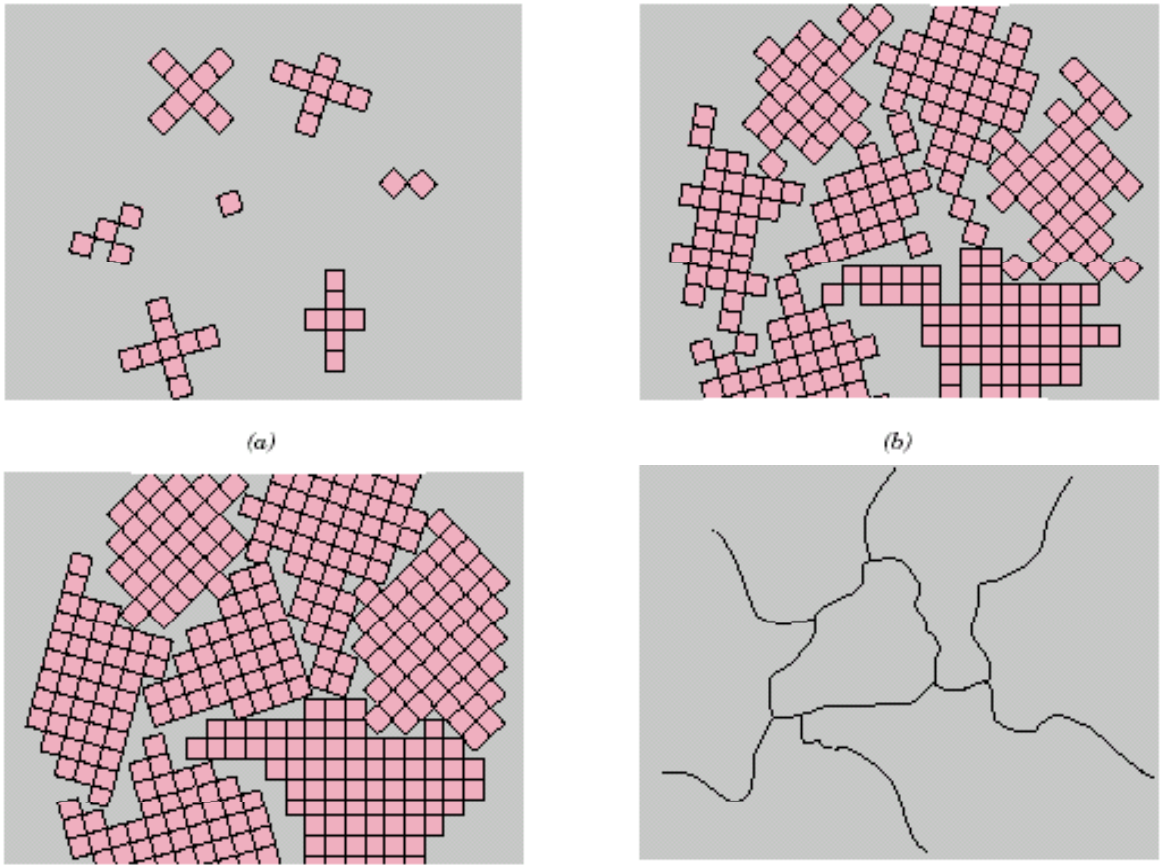
(110) 격자면

Crystalline / noncrystalline

- 단결정 (single crystal)
  → 전체 고체 결정내의 원자의 주기적, 규칙적 배열에 전혀 결함이 없는 경우
  → 성장이 어려움

FIGURE 3.32 Photograph showing several single crystals of fluorite, CaF_2. (Smithsonian Institution photograph number 38181P.)

- **다결정 (polycrystal)**
  - → 여러 개의 결정립(grain)들로 이루어진 결정체
  - → 결정립계(grain boundary) 형성



(a) (b) (c) (d)

- 이방성 (anisotropy)
  - → 물성이 결정학적 방위에 따라 달라지는 방향성
  - → 결정학적 방위에 따라 원자 또는 이온 간격이 달라지는 것에 관계
  - → 결정의 이방성은 결정구조의 대칭성에 의존
    - ⇒ 대칭성↓ → 이방성↑ (∴ 삼사정 → 이방성이 큼)
  - → 단결정에서 잘 나타나며
    다결정에서는 결정립의 무작위 배열로 등방성 (isotropic)을 띰
  - → 선택적 우선배향을 한 다결정 ⇒ 집합조직 (texture)

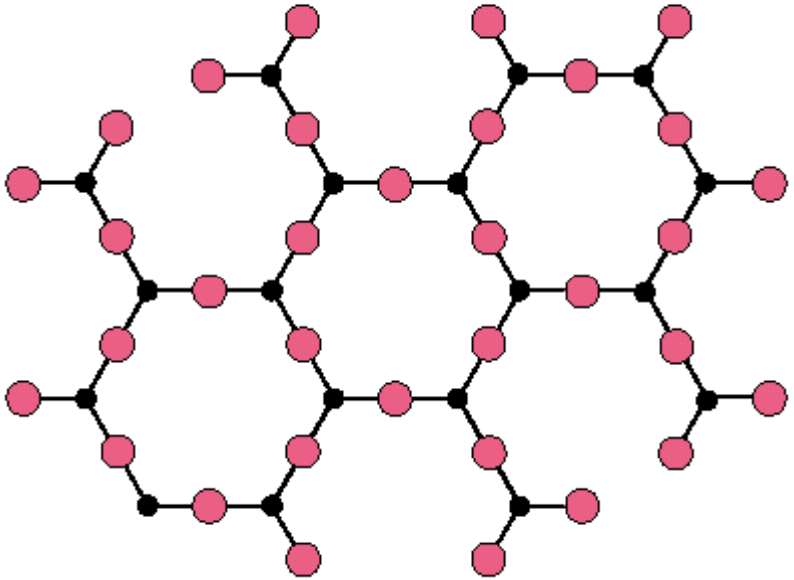
Table 3.7 Modulus of Elasticity Values for Several Metals at Various Crystallographic Orientations

	Modulus of Elasticity (GPa)		
Metal	[*100*]	[*110*]	[*111*]
Aluminum	63.7	72.6	76.1
Copper	66.7	130.3	191.1
Iron	125.0	210.5	272.7
Tungsten	384.6	384.6	384.6

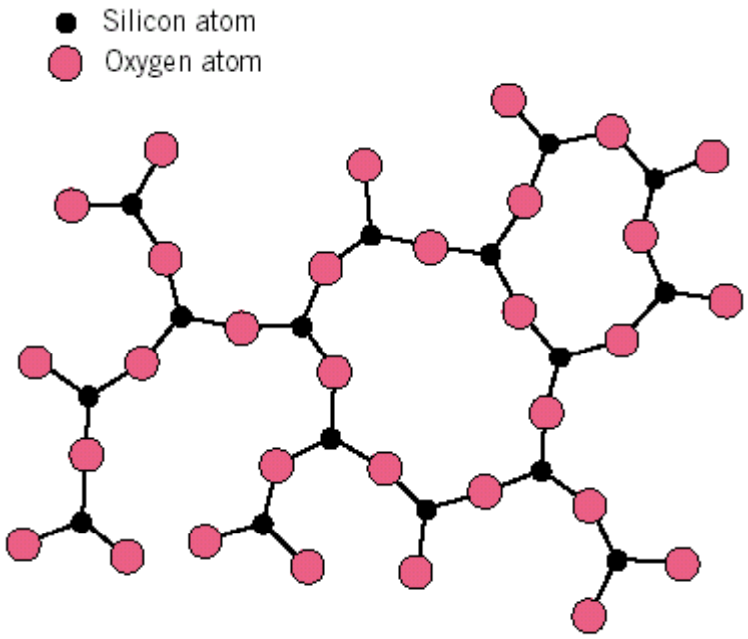
Source: R. W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd edition. Copyright © 1989 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

- **비정질 (noncrystalline materials)**
  → 고체 결정내의 원자배열에 주기성, 규칙성이 적은 경우
  → amorphous 또는 supercooled liquids

예) SiO_2

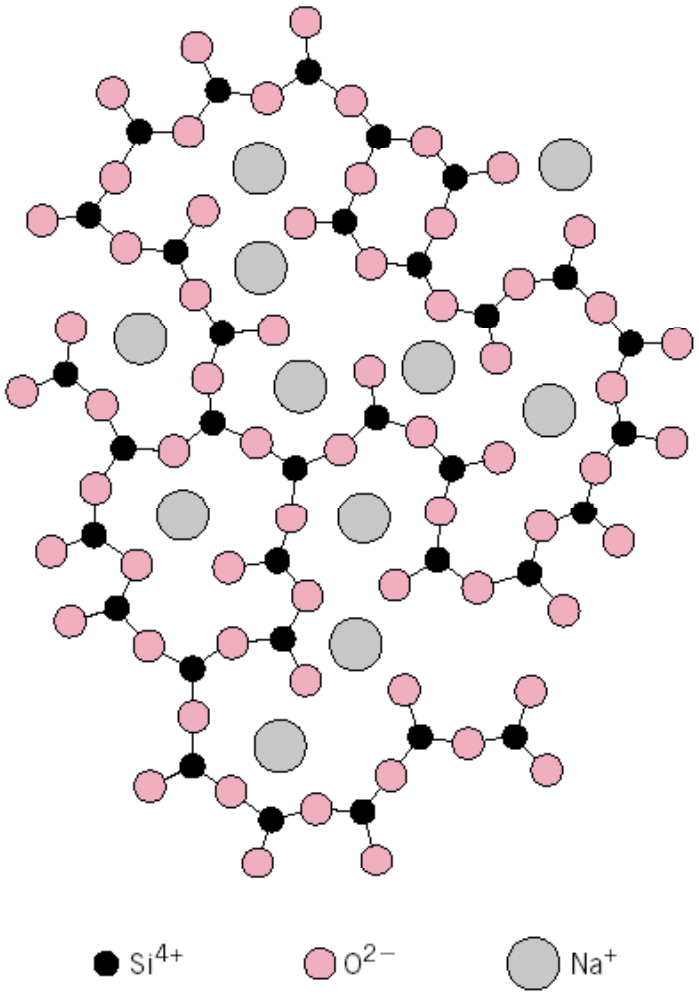


결정질 SiO_2



비정질 SiO_2

Silica Glasses



→ 비정질 silica (SiO_2)

→ fused silica 또는 vitreous silica

Network modifier

→ 양이온이 network을 조절

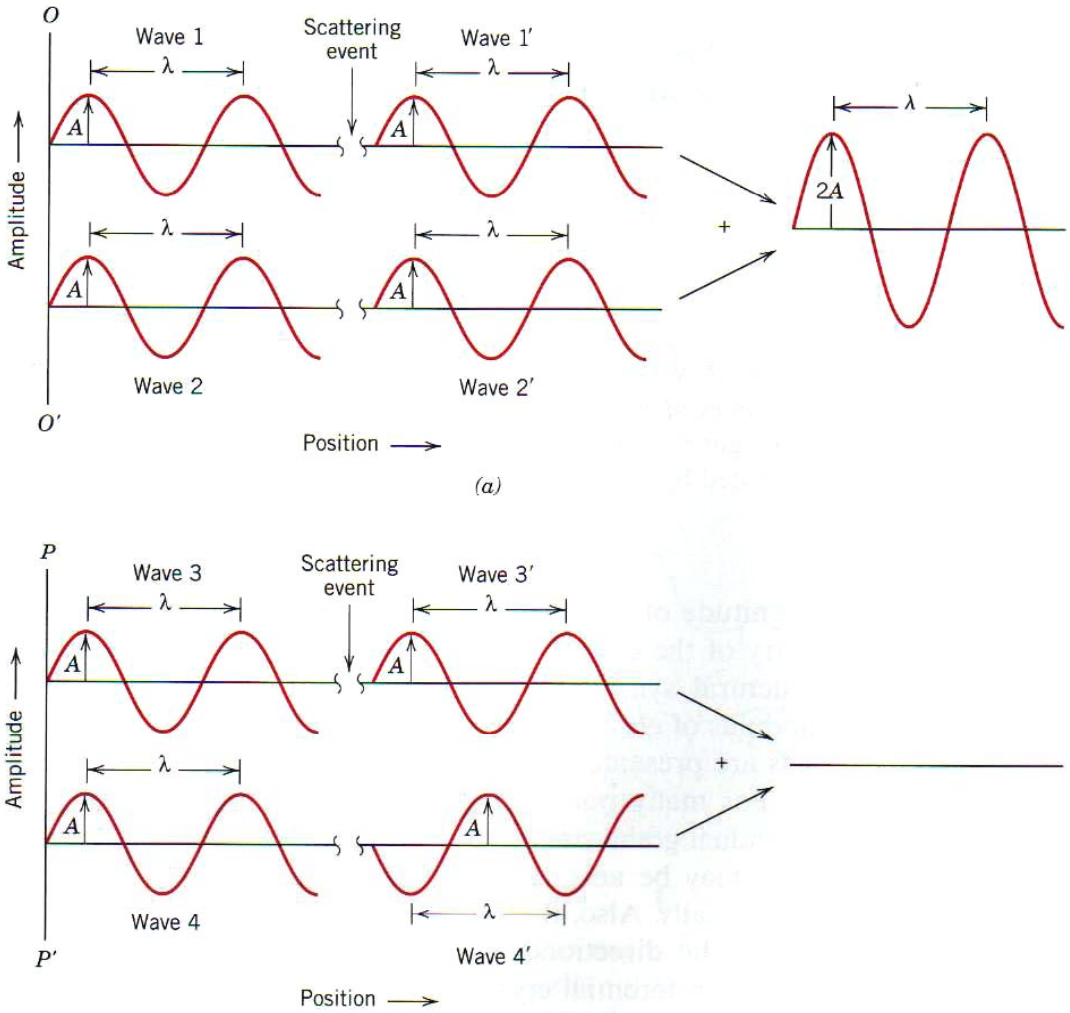
→ CaO, Na_2O

Intermediates

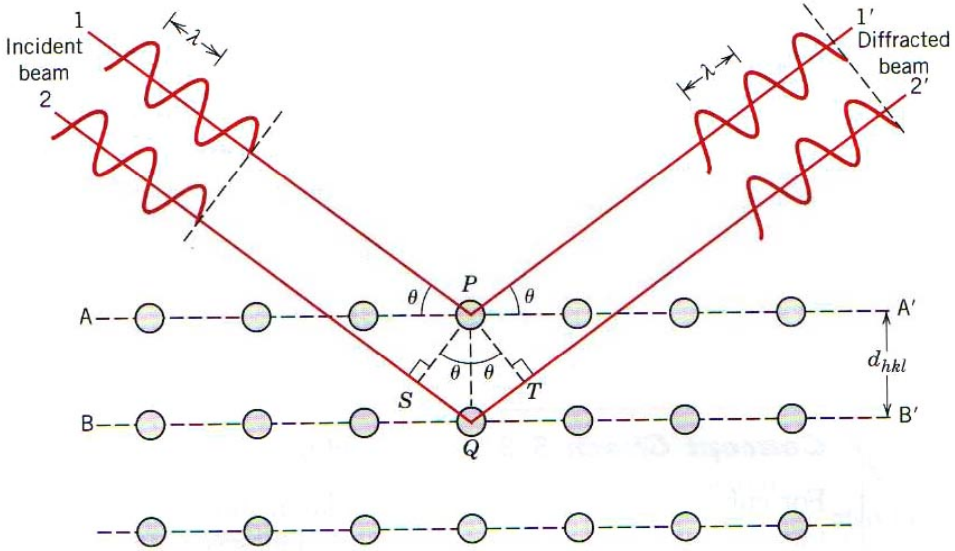
→ Si를 대체, network을 안정화

→ TiO_2, Al_2O_3

X-ray Diffraction



Bragg's Law

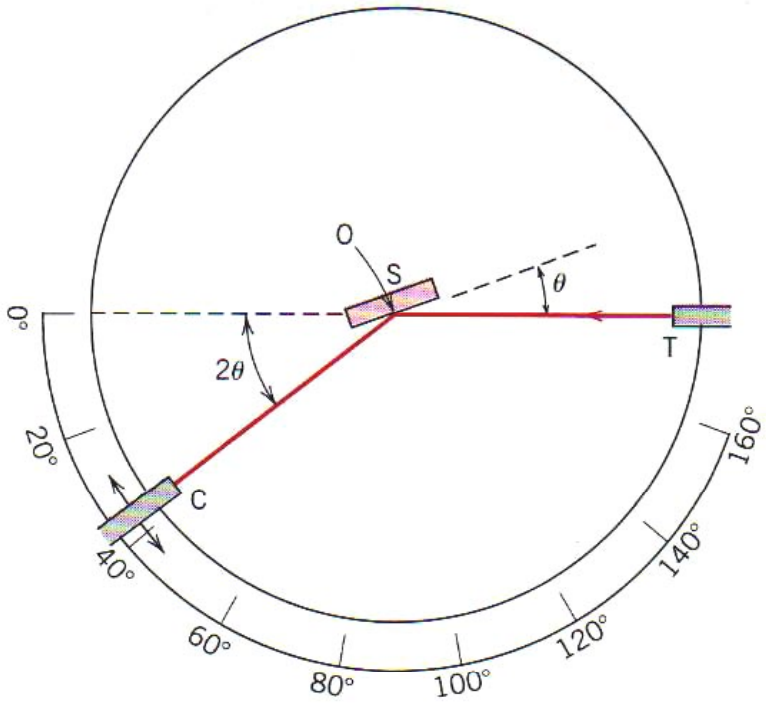


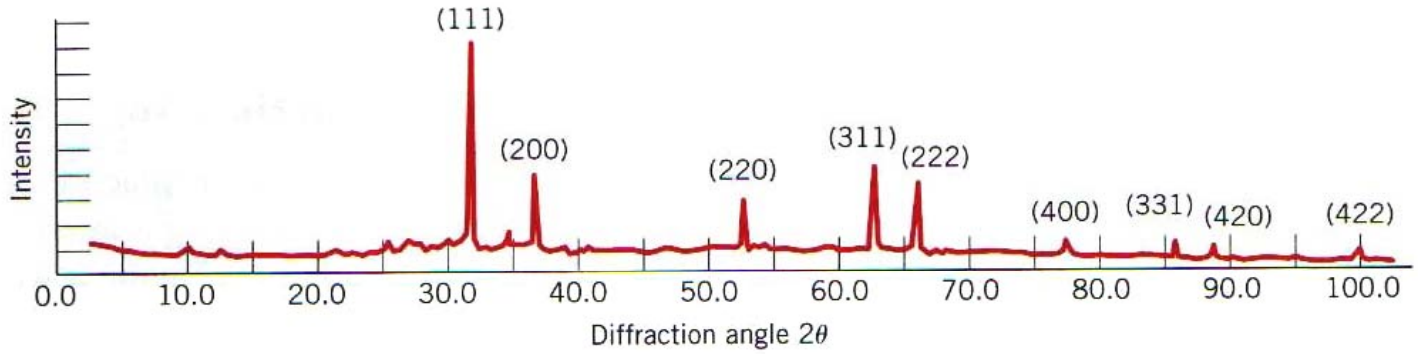
$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$= 2d_{hkl}\sin\theta$$

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


O
S
θ
T
2θ
C
0°
20°
40°
60°
80°
100°
120°
140°
160°


Intensity
(111)
(200)
(220)
(311)
(222)
(400)
(331)
(420)
(422)
0.0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
Diffraction angle 2θ

Ex) The lattice parameter of Fe = 0.2866 nm,

λ of X-ray source = 0.1790nm

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

$$d_{hkl} = \frac{0.2866}{\sqrt{2^2 + 2^2 + 0^2}} = 0.1013nm$$

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13^o$$