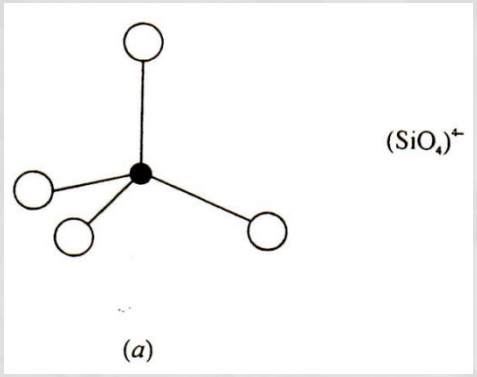
2-3-2 Silicate structure

- For the given stable radious of Si and O, if we calculate the coordination numbers of Si and O, they are 4 and 2, respectively.
- To satisfy the CN '4' for Si ion, Si is located on the center of tetrahedron and O atom is located on the vertex of it.
- This tetrahedron would prefer to share the vertex with other tetrahedron rather than the side or face of it



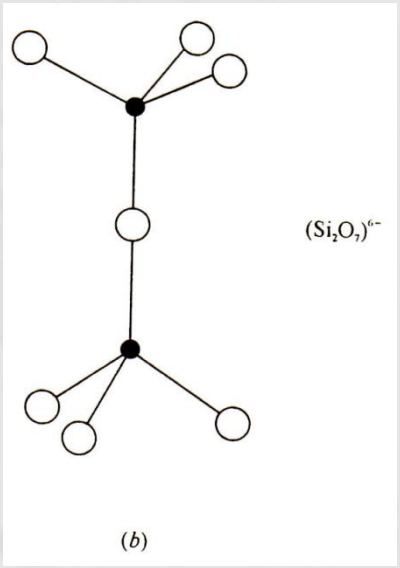


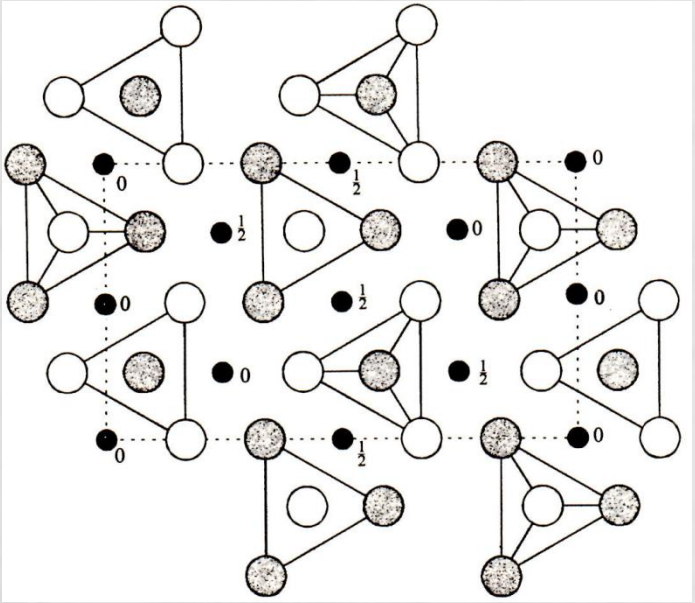
그림 2-18(a) 정규산염. 공유하는 꼭지점의 수가 0 이고 O/Si 비는 4이다.
(b) 파이로 규산염. 공유하는 꼭지저의 수가 1이고 O/Si 비는 3.5이다.

Figure 2-7 shows the classcification of the Si-O tetrahedron as the number of sharing vertex

표 2-7 사면체가 공유하는 꼭지점의 수에 따라 분류한 규산염.

공유 꼭지점의 수	Si-O 그룹	규산염	구조	
0	SiO_4	정규산염	사면체 하나	Orthosilicate
1	Si_2O_7	파이로규산염	사면체 쌍	Pyrosilicate
2	SiO_3	메타규산염	사슬 또는 고리	Metasilicate
5/2	Si_4O_{11}	이중사슬규산염	이중사슬	Double chain Silicate
3	Si_4O_{10}	판규산염	2 차원 판	Sheet silicate
4	SiO_2	망목규산염	3 차원 망목	Network silicate

- One of the example for orthosilicate is ‘olivine, (Mg, Fe)2SiO4’.
- Its crystal structure is given in the Fig. 2-19 and each tetrahedron is separated from each other.
- Positive Mg ions are surrounded by an octahedron that was formed by the 6 negative ions.



●: Mg ○: O

그림 2-19 포스터라이트의 구조. SiO_4 사면체가 떨어져 있다. 산소 원자는 높이 $\frac{1}{4}$ (회색)과 $\frac{3}{4}$ (흰색)에 있고 사면체 중심에 있는 Si 원자는 생략했다.

- If the number of sharing vertex is ‘2’, then the silicate structure is called by ‘metasilicate’ and the ratio O/Si is ‘3’.
- The metasilicate structure is given in Fig. 2-20.

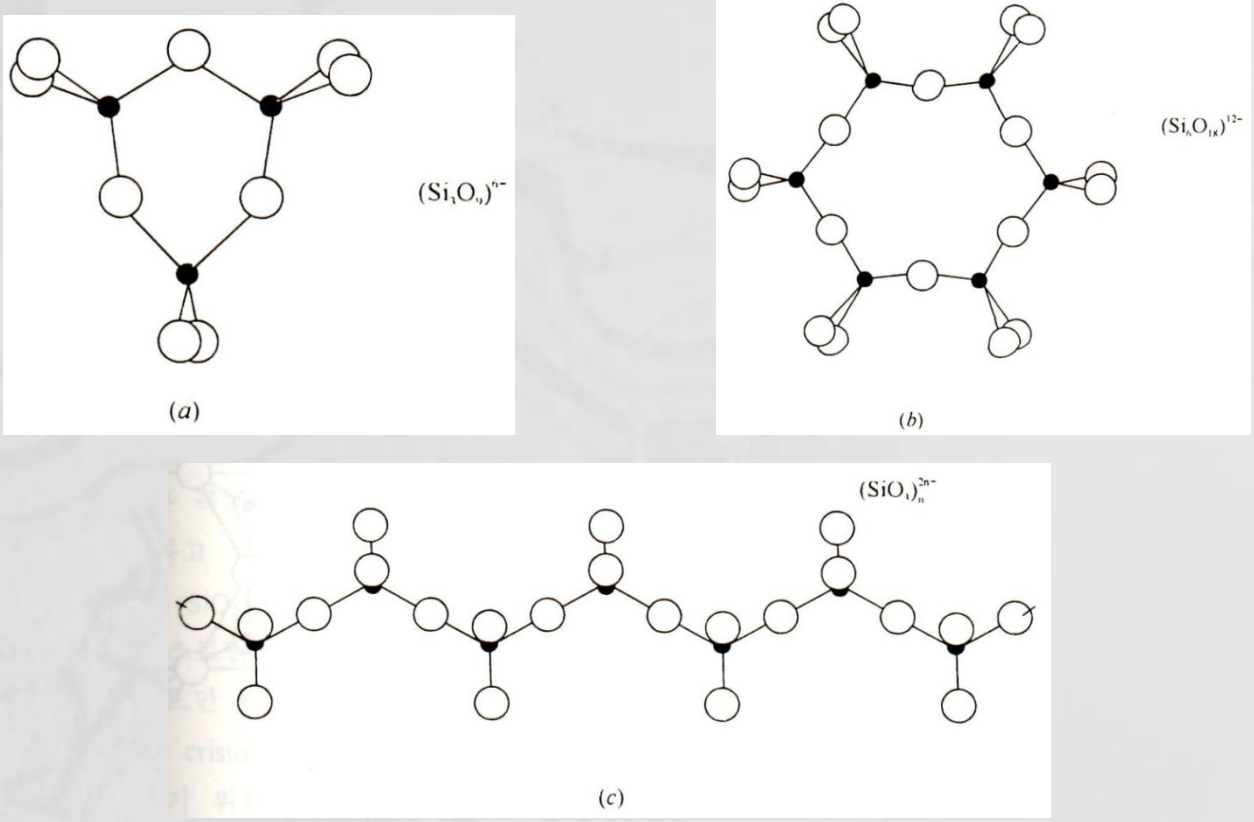
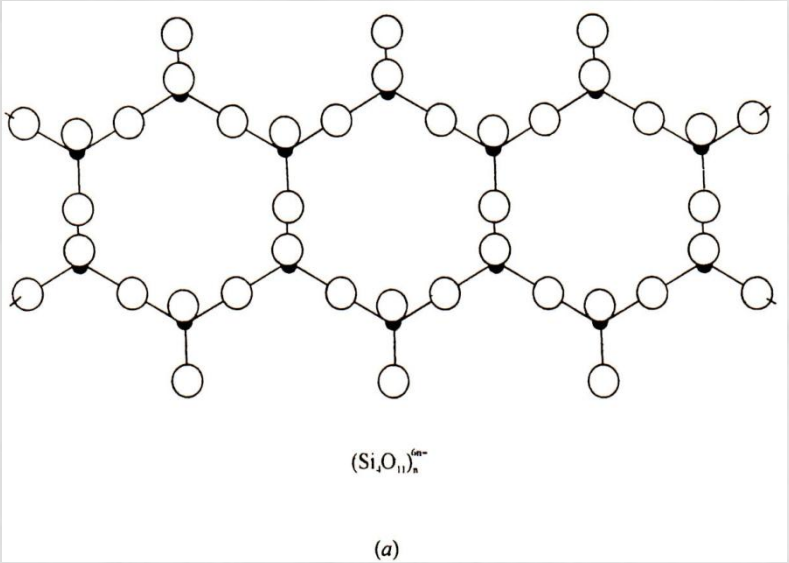


그림 2-20 메타규산염. 공유하는 꼭지점의 수가 2 이고 O/Si 비는 3 이다.

- If the number of sharing vertex is ‘5/2’, then the silicate structure is called by ‘double chain silicate’ and the ratio O/Si is ‘2.75’.
- The double chain silicate structure is given in Fig. 2-21(a).



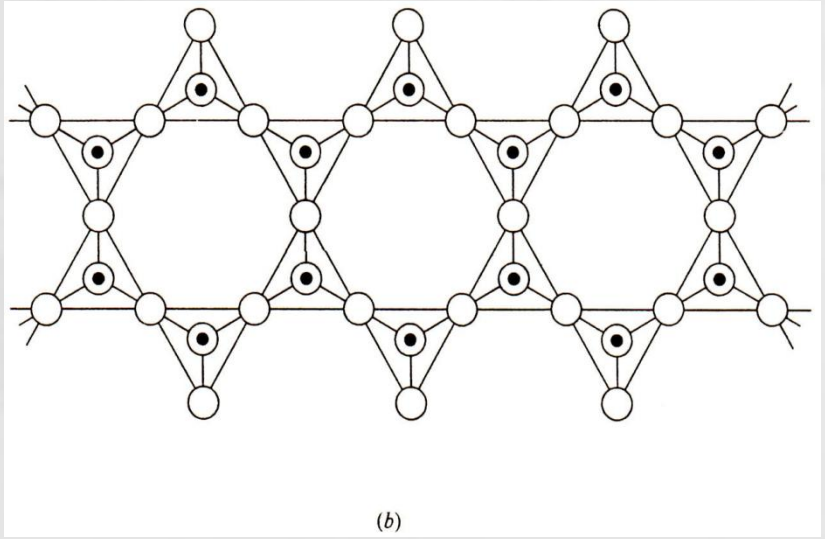
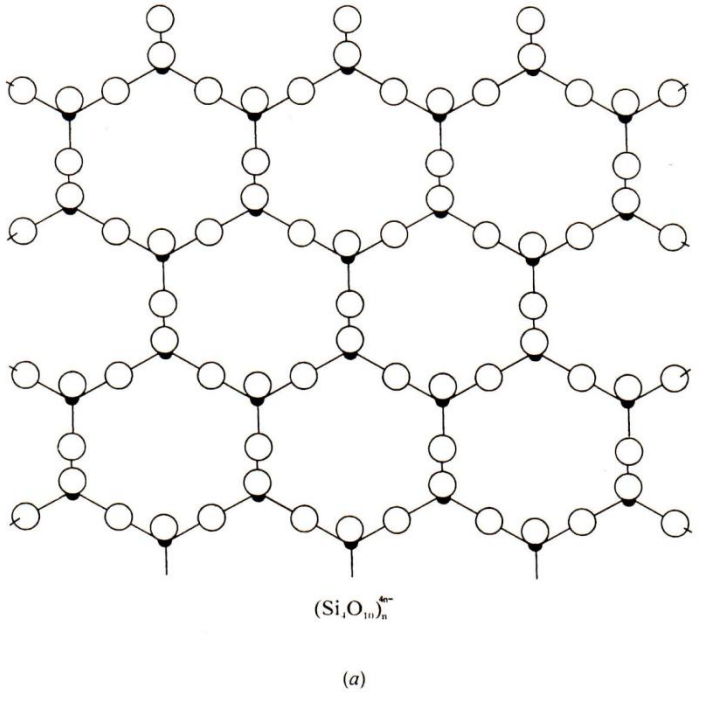


그림 2-21 이중사슬규산염. 공유하는 꼭지점의 수가 5/2 이고 O/Si 비는 2.75 이다.

- If the number of sharing vertex is '3', then the silicate structure is called by 'sheet silicate' and the ratio O/Si is '2.5'.
- The sheet silicate structure is given in Fig. 2-22(a) and (b).



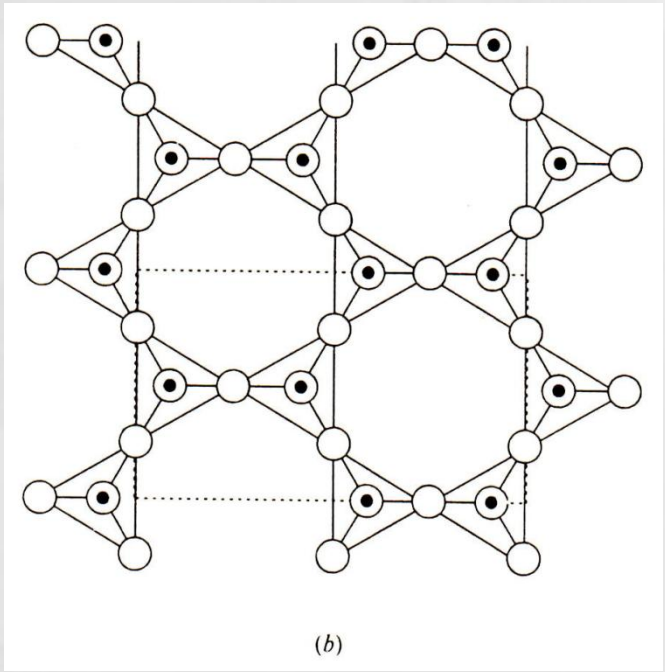


그림 2-22 판규산염. 공유하는 꼭지점의 수가 3 이고 O/Si 비는 2.5 이다.

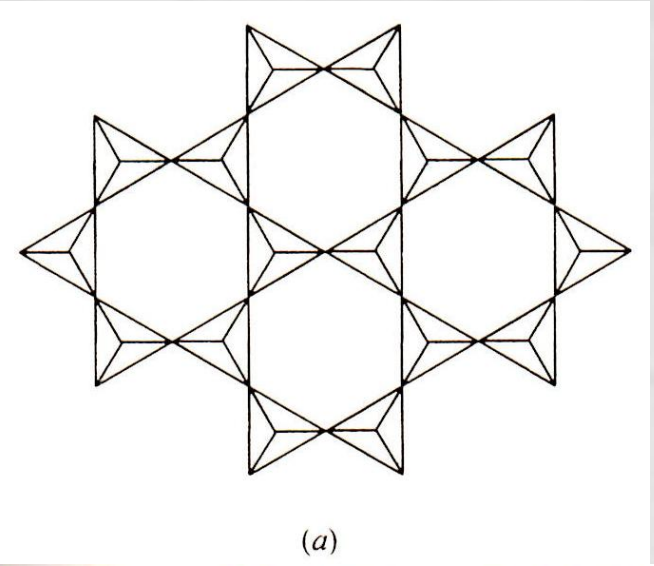
2-4. Amorphous oxide structure

- Amorphous structure is randon network structure.
- There is no symmetric or regular structure.

- There are suggested 4 rules to form the oxide amorphous.

1. Each oxide ions should be combined with less than 2 positive ions.
2. The coordination number of oxide ion surrounding the central positive ion is less than '4'.
3. The oxide polyhedron should share not the side or face but the vertex.
4. To form the 3-D structure, each polyhedron should share at least 3 vertices.

- Network former : the positive ions that can make continuously network like B, Si, Ge, P, V, As, Sb, etc.
- The CN for B is '3' and that for the others is '4'.
- Therefore, the possible oxide polyhedrons are triangle and tetrahedron.
- There are intermediate (Al, Pb, Zn, Be) and network modifier (Zn, Ba, Ca, Na, K).



VS

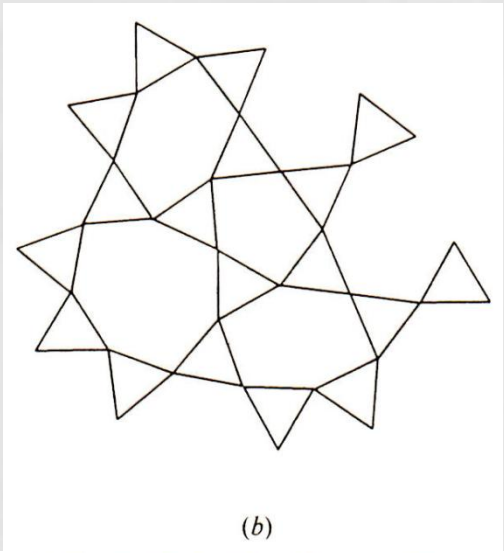


그림 2-25 (*a*) 결정질 산화규소를 2 차원으로 나타낸 그림, (*b*) 비정질 산화규소를 2 차원으로 나타낸 그림.

- For pure SiO2 glass network structure, each Si atom is surrounded by the 4 oxide ions and each oxide ion is connected with the 2 Si ions, so there is no dangled binding.
- Therefore, the quartz fused by the pure SiO2 has very high glass transition temperature and it is very strong glass against the thermal impact.
- If the glass transition temperature(softening temp.) is too high, the manufacturing cost will be very high.
- To decrease the glass transition temperature, we need to make a weak binding by breaking the tetrahedron network using network modifier (Na2O, CaO, B2O3, etc.)

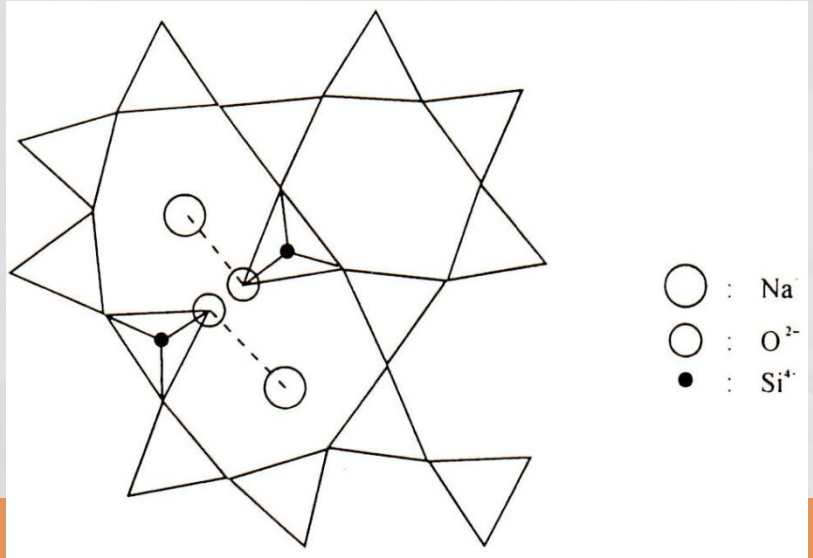


그림 2-26 비정질 산화규소에 Na2O가 들어가서 망목을 끊는 모습을 나타낸 그림.

Homework #2.

- Solve the following problems.
- Exercise #2-3,5, 7, 8, 14, 17, 21, 27

3. 어떤 원소가 다음과 같은 전자 배치를 지니고 있을 때 다음의 물음에 답하시오.

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^2$

(a) 이 원소로 이루어진 결정은 무슨 결합을 갖는지 답하시오.

(b) 예상되는 결정 구조를 그리고 설명하시오.

(c) 어떤 성질을 갖는지 설명하시오.

5. 같은 원자로 배위수가 3 이 되도록 2 차원에서 계속 연결하면 어떤 구조가 되는지 설명하시오.

7. 조밀 충전이란 무엇인가? 육방 조밀 충전에서 c/a 의 값을 구하시오.

8. 다음의 구조에서 채움율을 계산하시오.

(a) 단순 입방 구조

(b) 면심 입방 구조

(c) 체심 입방 구조

(d) 정사면체의 꼭지점에 중심을 두고 충전되어 있는 경우 이 정사면체에서의 채움율

14. 이온 결합에서 배위수에 영향을 주는 요인 세 가지를 쓰고 설명하시오.

17. 같은 원자로 배위수가 6 이 되도록 계속 충전하면 무슨 구조가 되는지 설명하시오. 두 종류의 원자로 배위수가 모두 6 이 되도록 계속 충전하면 무슨 구조가 되는지 설명하시오.

21. 어떤 가상의 화합물 AB 에서 각 A 이온이 12 개의 A 이온과 6 개의 B 이온을 접하고 있다면 이 화합물에서 두 이온의 반경비를 구하시오. 또 이 화합물의 결정 구조를 그리고 설명하시오.

27. 결정과 유리의 구조적 차이를 설명하시오.

29. 결정을 비정질 구조로 만드는 방법 3 가지를 들고 설명하시오.

Chapter 3. Lattice and Symmetry

Contents

3-1. Lattice and Unit Cell

- The crystal is a solid system that has periodic atomic arrays.
- So the crystal system has symmetry in the periodic regularity.
- There are several symmetry factors.
- At first, 2-dimensional atomic arrays will be discussed and then the discussion will be extended to 2-dimensional atomic arrays.
- Fig. 3-1 shows the 2-dimensional crystal that has a layer of carbon atoms to make graphite.

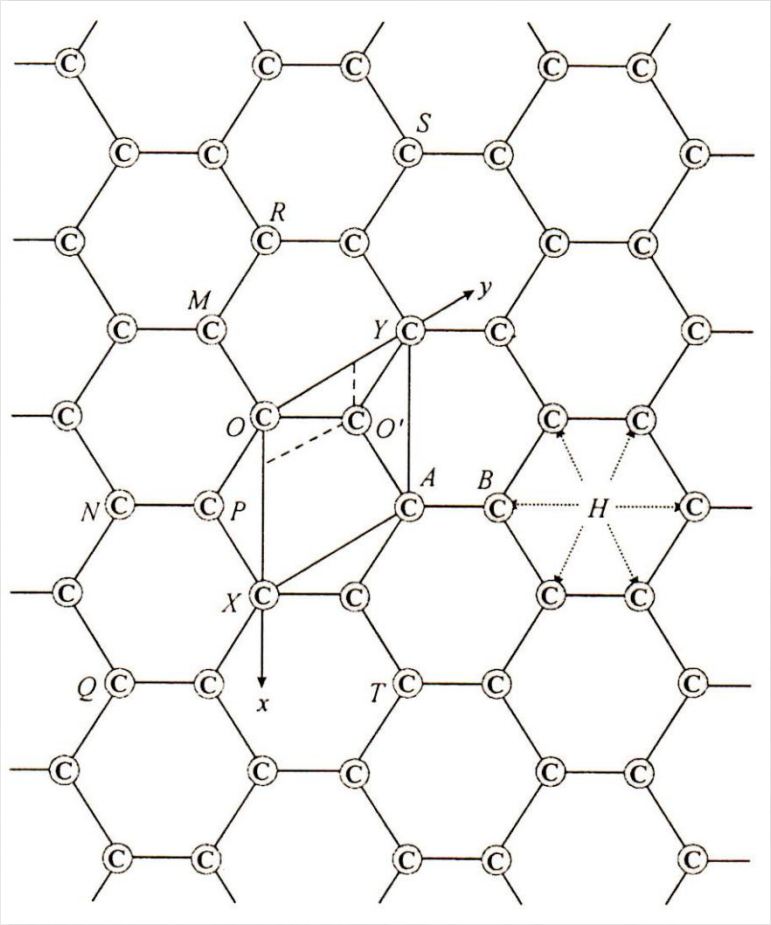


그림 3-1 세 개의 최인접 원자를 가진 흑연 층상구조에서 한 층의 원자배열을 보여주는 개략도.

- All the carbon atoms have coordination number '3'.
- But, number of type to array the atoms are '2', A and B that have different direction for array of neighboring atom.
- The atoms located on the N, Q sites are on the same situation as atom 'A'.
- Also, the atoms located on the M, P sites are on the same situation as atom 'B'.
- There is '**unit cell(단위포)**' that is defined by a **parallelogram(평행사변형)** OXAY in a 2-dimension.
- The unit cell will be extended to **a parallelepiped(평행육면체)** for 3-dimension.

- In a 2-dimensional space, **mesh or net** can be defined by the array of the points that have **periodic surrounding**.
- In 3-dimensional space, the periodic structure is called by **lattice** and each points are called by **lattice point**.
- Figure 3-2 is the lattice that can be acquired from the array of carbon atoms of Fig. 3-1.
- The **'translational symmetry'** is defined by the periodic symmetry in the lattice as shown in Fig. 3-2.

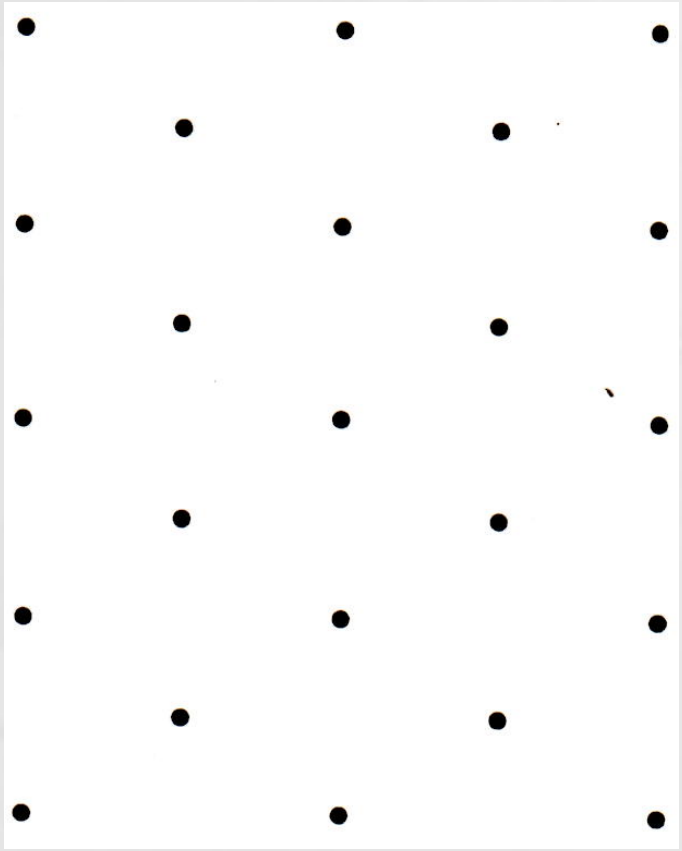
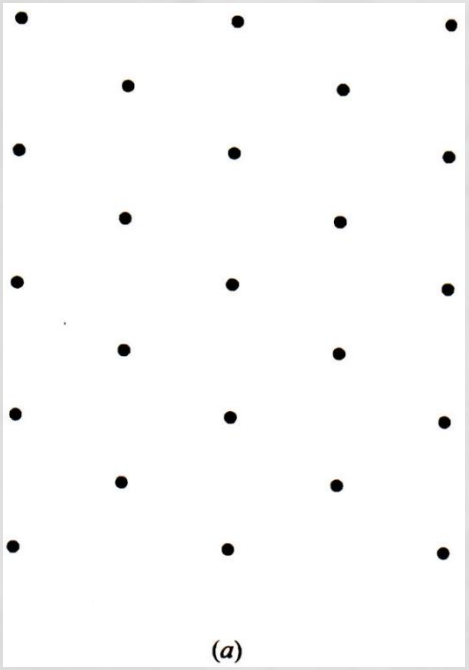
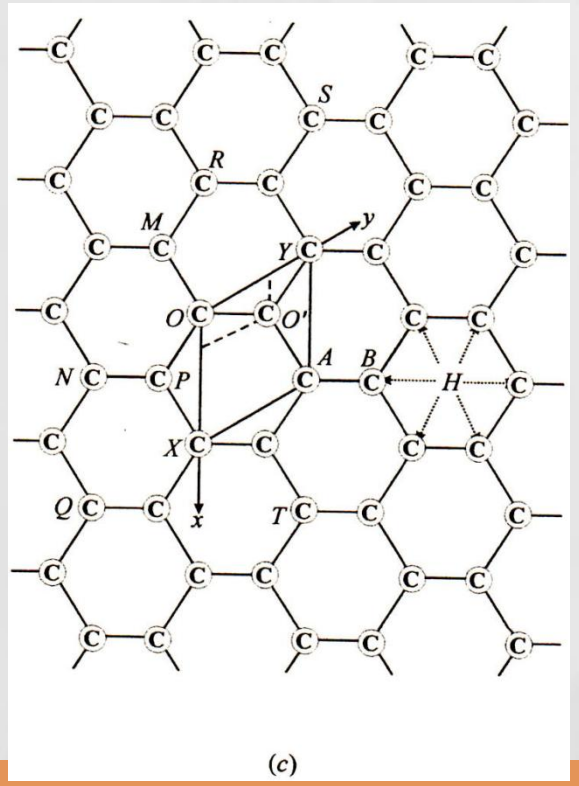


그림 3-2. 그림 3-1의 2차원 원자 배열에서 얻어진 격자.

- The '**basis**' is defined by the group of atoms that formed the whole crystal by locating at all lattice points.
- Figure 3-3 shows that the whole crystal structure(3-3(c)) can be expressed by **the combination of lattice points (3-3(a)) and basis (3-3(b))**.





- As shown in Fig. 3-4, we can make the various **parallelograms** as we connect the lattice points.
- By moving these parallelograms parallel, the whole space can be occupied.
- There is '**unit cell**' that is defined by a **parallelogram** in a 2-dimension and **a parallelepiped** for 3-dimension.

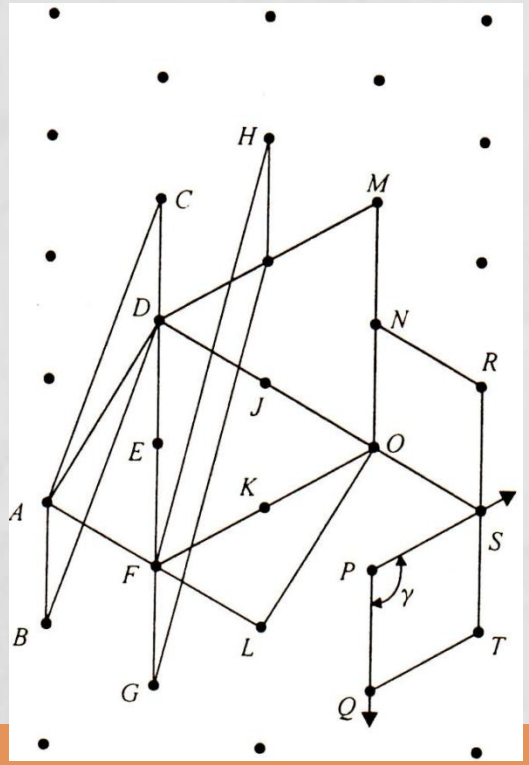


그림 3-4. 2차원에서의 여러 단위포인 평행사변형.

- **'The primitive unit cell'** is defined by the unit cell that has only one lattice point.
- For example, the **parallelogram** ABCD in Fig. 3-4 is the primitive unit cell.
- But, for the **parallelogram** ALOD, it is 'nonprimitive unit cell, because it has more than one lattice point.

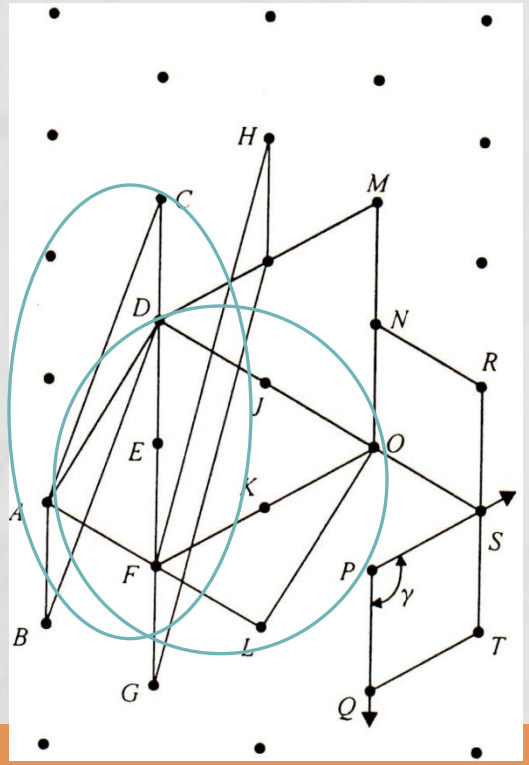
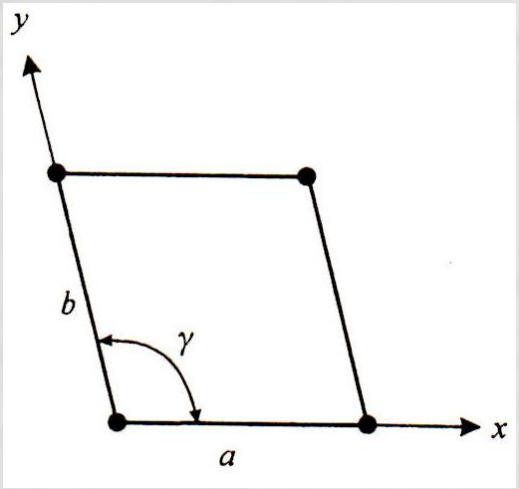


그림 3-4. 2차원에서의 여러 단위포인 평행사변형.

- The unit **parallelogram** in 2-dimensional space can be expressed by two sides a and b, and the angle between those sides as shown in Fig. 3-5(a).
- For 3-dimensional space, the unit cell will be extended to **a parallelepiped,** the origin of coordination system will be vertex of parallelepiped and the sides of parallelepiped will be the x, y, z axis of crystal.
- As shown in Fig. 3-5(b), angle α, β, γ are called by **'axial angle'**, the space a, b, and c, between lattice points along x, y, and z-axis are called by **'lattice parameter'.**

(a)



(b)

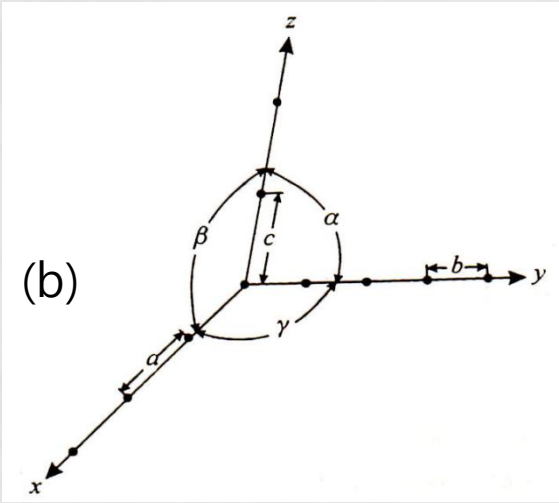


그림 3-5 (a) 2차원에서의 단위포, (b) 3차원에서의 단위포.

- For example, if we figure out the unit cell and lattice of CsCl(cesium chloride), already discussed in Fig. 2-14, then it is cubic unit cell with a=b=c and $\alpha=\beta=\gamma=90^\circ$.

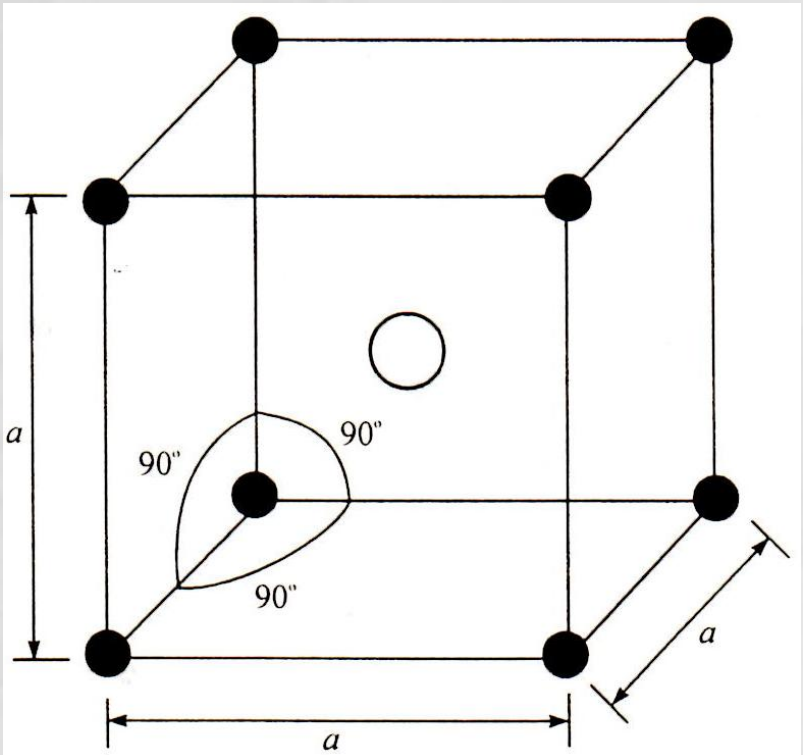


그림 2-14 염화세슘(CsCl) 구조.

Cl atom : (0, 0, 0)
Cs atom : (1/2, ½, ½)