基礎固態化學

Class No.: E3186

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Textbook

"Basic Solid State Chemistry", 2nd ed. West, A. R.

Wiley

Syllabus

Chapter 1 Crystal Structure

Chapter 2 Bonding in Solids

Chapter 3 Crystallography and Diffraction Techniques

Chapter 4 Other Techniques: Microscopy, Spectroscopy, Thermal Analysis

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Final Presentation 15%

Chapter 1 Crystal Structures

Many of the properties and applications of crystalline inorganic materials revolve around a small number of structure types
→ We must first consider some basic concepts of crystallography for structure description.

1.1 Unit cells and crystal systems

Crystal: regular arrangements of atoms in three dimensions

represented by a repeating unit or motif

unit cell

Unit cell: the smallest repeating unit showing the full symmetry of the crystal structure.

first consider 2D, Fig.1.1(a); possible repeat units (b)–(e)
NaCl
Adjacent squares share edges and corners

The choice of origin of the repeat unit:

1. personal taste
2. NaCl is usually chosen as (b) or (c), rather than (d)

   easier to draw and visualize,
   contain atoms at special positions,
   corners, edge centers,…
3. symmetry is evident

Comparing (e) with (b) and (c)

a. the units in (e) are half the size of those in (b) and (c)

   ∴ (e) is preferred in 2D

b. In 3D, however, (c) is preferred because it shows the cubic symmetry.

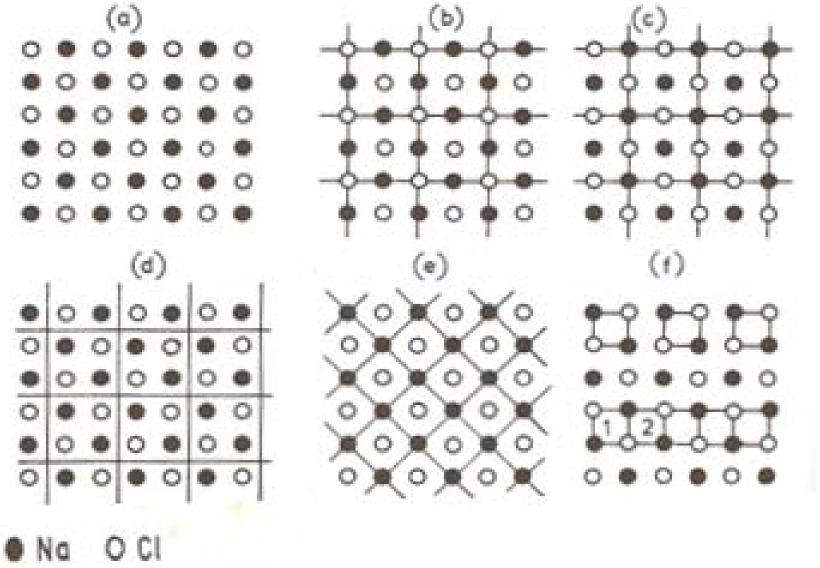


Fig. 1.1 (a) Section through the NaCl structure, showing: (b) to (e) possible repeat units; and (f) incorrect units

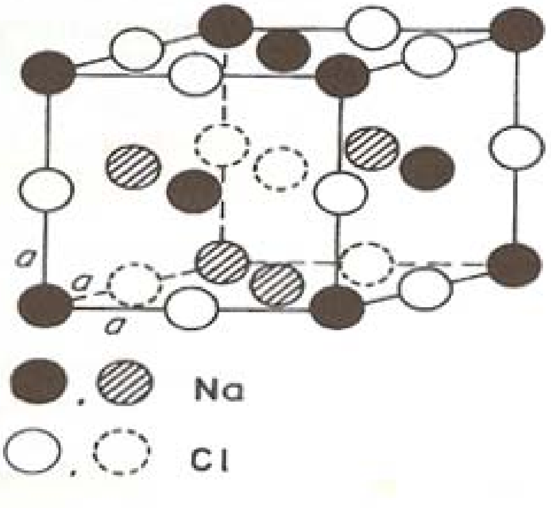


Fig. 1.2 Cubic unit cell of NaCl, $a = b = c$

(f) shows examples of what is not a repeat unit

- a. (top) the squares are identical, but it is not permissible to isolate unit cells
- b. (bottom) it contains units that are not identical (1 and 2)

Fig.1.2 shows the unit cell of NaCl in 3D:

- a. Na: corner and face center positions
- b. Cl : edge centers and body centers
- c. the unit cell is cubic
  - $a = b = c$ in length for the three edges
  - $\underline{\alpha} = \underline{\beta} = \gamma = 90^\circ$ for the three angles

between b&c

between a&c

Table1.1 and Fig 1.3: Seven Crystal Systems

7 possible shapes

governed by the presence or absence of symmetry

1.2 Symmetry

Rotation axis, n

Fig.1.4(a) Silicate tetrahedron

the vertical Si–O bond as the axis

- a. every 120° the tetrahedron finds itself in an identical position.
- b. different identical positions are possible → possess symmetry
- c. the axis is a rotation axis
  this is an example of a *symmetry element*;
  the process of rotation is a *symmetry operation*.

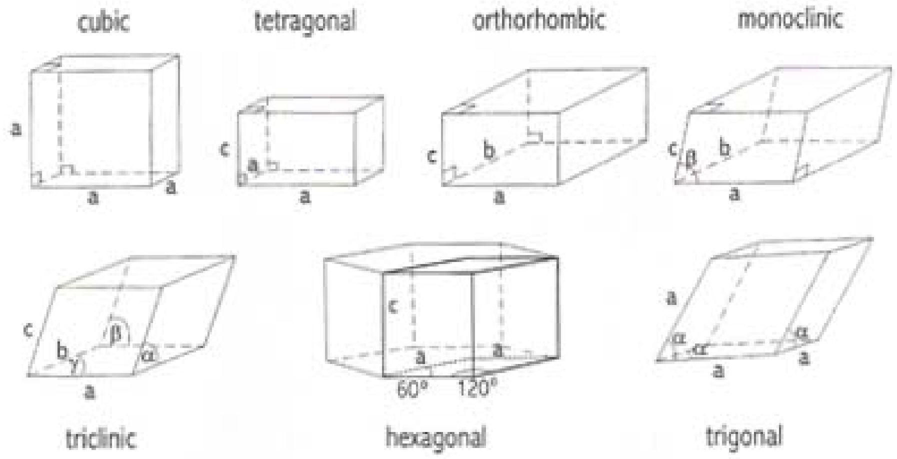


Fig. 1.3 The seven crystal systems and their unit cell shapes

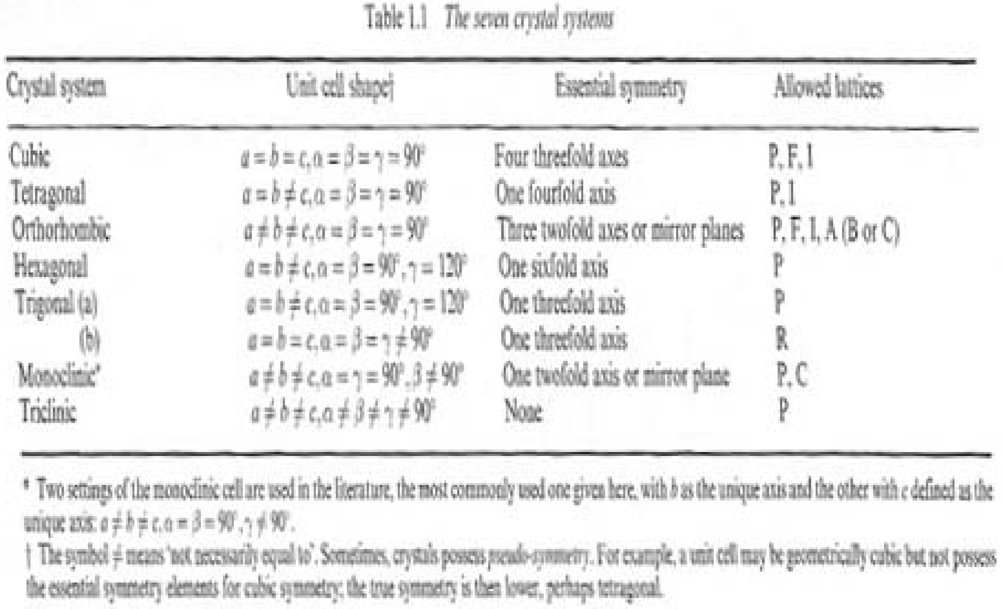


Table 1.1 *The seven crystal systems*

Crystal system	Unit cell shape†	Essential symmetry	Allowed lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90°$	Four threefold axes	P, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90°$	One fourfold axis	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90°$	Three twofold axes or mirror planes	P, F, I, A (B or C)
Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P

* Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with b as the unique axis and the other with c defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90°, \gamma \neq 90°$.

† The symbol $\neq$ means 'not necessarily equal to'. Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

Table1.2 shows different symmetry elements

Fig.1.4 (a) SiO_4

A rotation axis, n, and by 360/n degrees gives an identical orientation; the operation is repeated n times before the original configuration is regained.

$\therefore$ $n = 3$, the axis is a threefold rotation axis.

SiO_4 tetrahedron possesses four threefold rotation axes.

Fig.1.4 (b) SiO_4

twofold rotation axes, passing through the central Si and bisect the O–Si–O bonds; SiO_4 tetrahedron possesses three twofold axes.

Rotational symmetry can be $n = 2$, 3, 4 and 6

$n = 5$, 7 are never observed

a molecule can have pentagonal symmetry ($n = 5$), but their fivefold symmetry cannot be exhibited by the crystal as a whole (Fig.1.4(c)).

Fig.1.4(d) shows sixfold rotation axes.

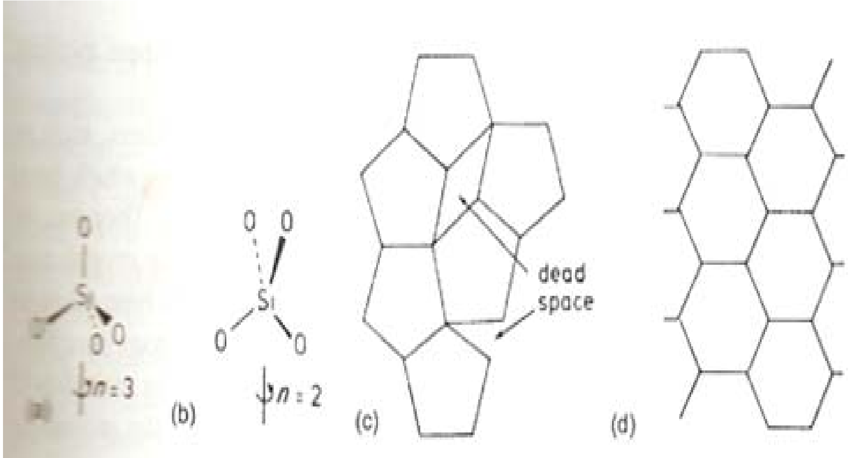


Fig. 1.4 (a) Threefold and (b) twofold rotation axes. (c) The impossibility of forming a complete layer of pentagons. (d) A complete layer of hexagons

Mirror plane, m

Two halves of , for instance, a molecule can be interconverted by carrying out the imaginary process of reflection across the mirror plane. The SiO_4 tetrahedron possesses six mirror planes

Fig.1.5(a): silicon and oxygens 1 and 2 lie on the mirror plane; 3,4 are interchanged on reflection. A second mirror plane lies in the plane of the paper; Si and 3,4 lie on the mirror but 2, in front of the mirror, is the image of 1, behind the mirror.

Center of symmetry, $\bar{1}$

The center of symmetry is a point and an identical arrangement can be found on the other side.

An AlO_6 octahedron has a center of symmetry located on the Al atom. (Fig.1.5 (b), Al as the center, oxygen 2 can be obtained from 1 by extending an equal distance on the other side.)
SiO_4 dose not have a center of symmetry.

Inversion axis, $\bar{n}$

a symmetry operation involves rotation and inversion through the center; Fig.1.5(c), Oxygens 2 and 3 are related by a $\bar{4}$ (fourfold inversion) axis, i.e. 2 is rotated by 360/4 = 90° (to position 2') and then taken by inversion through the center to position 3.

$\bar{1}$ is simply equivalent to the center of symmetry.

The two fold inversion axis is the same a mirror plane perpendicular to that axis.

Point Symmetry:

- the symmetry elements discussed so far
- at least one point stays unchanged during symmetry operation

- finite-sized molecules can only possess point symmetry elements

Space Symmetry:

Crystals have extra symmetries, including translation steps

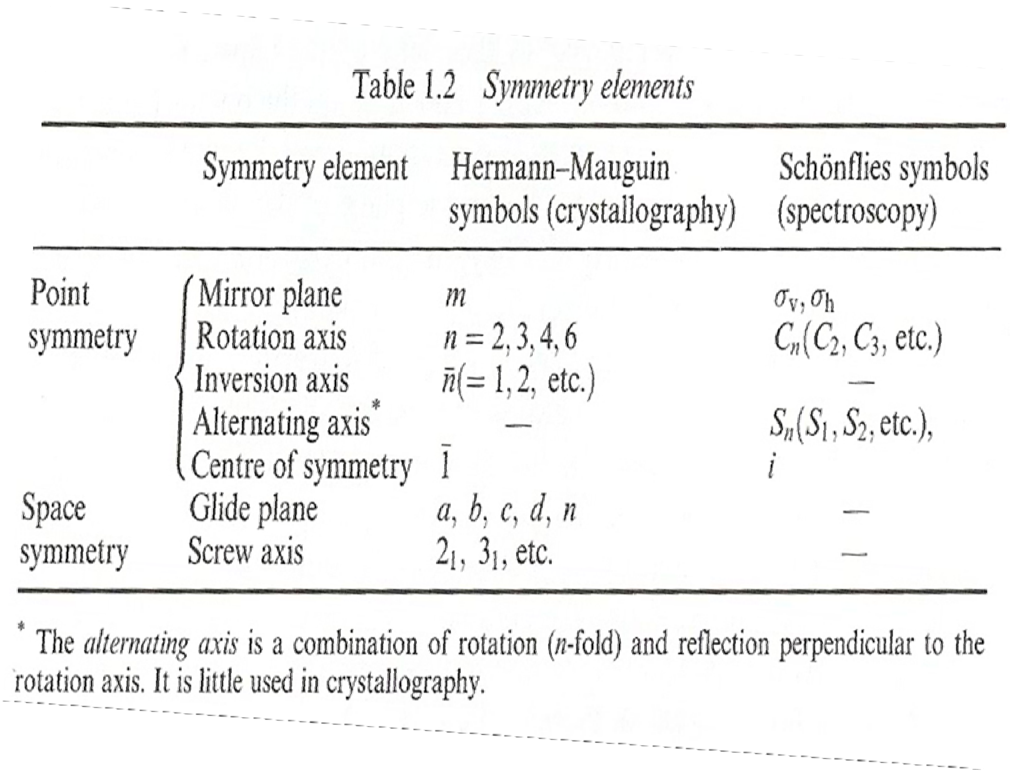


Table 1.2 *Symmetry elements*

	Symmetry element	Hermann–Mauguin symbols (crystallography)	Schönflies symbols (spectroscopy)
Point symmetry	Mirror plane	m	σ_v, σ_h
	Rotation axis	$n = 2, 3, 4, 6$	$C_n (C_2, C_3$, etc.)
	Inversion axis	$\bar{n}$(= 1, 2, etc.)	—
	Alternating axis*	—	$S_n (S_1, S_2$, etc.),
	Centre of symmetry	$\bar{1}$	i
Space symmetry	Glide plane	a, b, c, d, n	—
	Screw axis	2_1, 3_1, etc.	—

* The *alternating axis* is a combination of rotation (n-fold) and reflection perpendicular to the rotation axis. It is little used in crystallography.

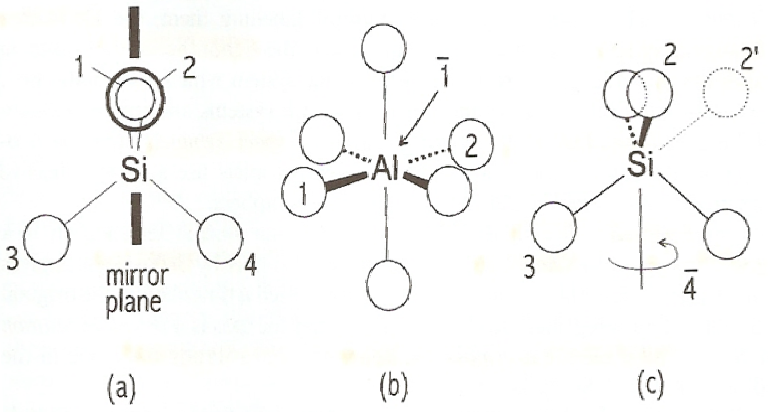
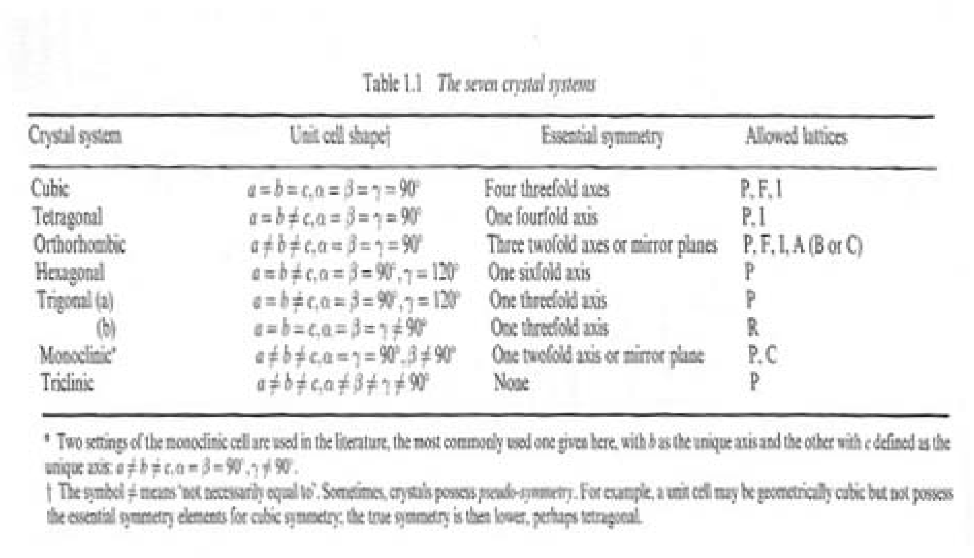


Fig. 1.5 Symmetry elements: (a) mirror plane; (b) centre of symmetry; (c) fourfold inversion axis

1.3 Symmetry and choice of unit cell

Table1.1 the seven crystal systems



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Hexagonal	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One sixfold axis	P
Trigonal (a)	$a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$	One threefold axis	P
(b)	$a = b = c, \alpha = \beta = \gamma \neq 90°$	One threefold axis	R
Monoclinic*	$a \neq b \neq c, \alpha = \gamma = 90°, \beta \neq 90°$	One twofold axis or mirror plane	P, C
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90°$	None	P

* Two settings of the monoclinic cell are used in the literature, the most commonly used one given here, with *b* as the unique axis and the other with *c* defined as the unique axis: $a \neq b \neq c, \alpha = \beta = 90°, \gamma \neq 90°$.

† The symbol $\neq$ means 'not necessarily equal to'. Sometimes, crystals possess *pseudo-symmetry*. For example, a unit cell may be geometrically cubic but not possess the essential symmetry elements for cubic symmetry; the true symmetry is then lower, perhaps tetragonal.

Cubic

Shape essential symmetry elements–by which crystal system is defined.

a＝b＝c Four threefold axes

$\alpha = \beta = \gamma = 90°$ (run parallel to the cube diagonals)

Fig.1.2 NaCl additional symmetry elements

Fig.1.6 (a) three fourfold axes Fig.1.6 (a)

mirror planes Fig.1.6 (b,c)

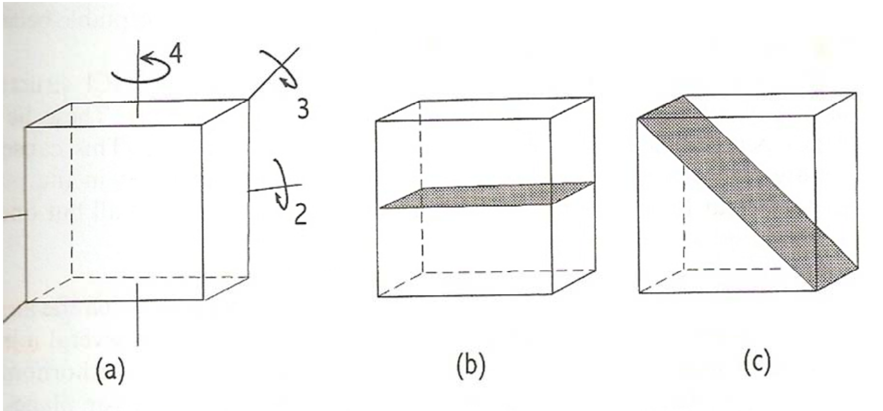


Fig. 1.6 (a) Two-, three-, and fourfold axes and (b, c) mirror planes of a cube

Shapes do not define the unit cells; they are a consequence of the presence of certain symmetry elements.

Tetragonal

Essential symmetry

$a = b \neq c$

single fourfold axis

$\alpha = \beta = \gamma = 90^\circ$

Fig.1.7 (a) CaC_2

$C{\equiv}C$

carbide ion is cigar-shaped, c-axis the unique one

- a cube that is either squashed or elongated along one axis

∴ all threefold axes and two of the fourfold axes are lost

- the choice of a tetragonal unit cell for NaCl (Fig.1.7 (b) (Fig.1.1 (e)) is rejected, even if the tetragonal has half the volume of the cube.
  (Cubic is always preferred)

Trigonal

Essential symmetry

$a = b = c$

single threefold axis

$\alpha = \beta = \gamma \neq 90^0$

Fig.1.7(c) $NaNO_3$

- a cube by stretching or compressing the cube along one of its body diagonals

∴ only one threefold axis parallel to this direction is retained, but others are destroyed

It is possible to describe such a trigonal cell for NaCl with $\alpha = \beta = \gamma = 60^\circ$ with Na at the corners and Cl in the body center. This is unacceptable because cubic NaCl has symmetry higher than trigonal.

Hexagonal

$a = b \neq c$

Essential symmetry

$\alpha = \beta = 90^\circ, \ \gamma = 120^\circ$

one sixfold axis (discussed later, Fig.1.17)

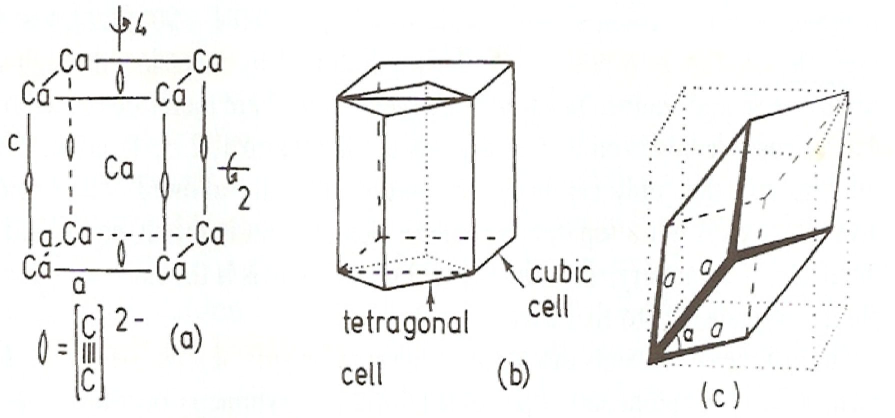


Fig. 1.7 (a) Tetragonal unit cell of CaC_2: note the cigar-shaped carbide ions are aligned parallel to *c*; (b) relation between 'tetragonal' and cubic cells for NaCl; (c) derivation of a primitive trigonal unit cell for NaCl from the cubic cell

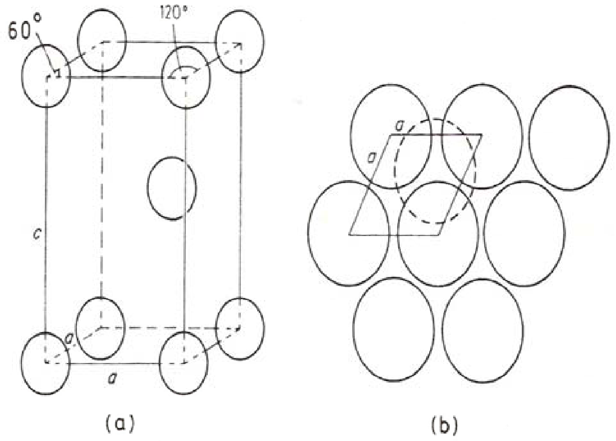


Fig. 1.17 Hexagonal unit cell of a *hcp* arrangement of spheres

Orthorhombic

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90^{o}$,

a shoebox

Essential symmetry
three mutually perpendicular
mirror planes
or
three mutually perpendicular two fold axes

the angles are 90º but the sides are of unequal length

Monoclinic

$a \neq b \neq c$

$\alpha = \gamma = 90^{o}$, $\beta \neq 90^{o}$

Essential symmetry
a mirror plane
or/and
a twofold axis

➢ derived from orthorhombic shoebox by partially shearing the top face relative to the bottom face and in a direction parallel to one of the box edges.

∴ most of the symmetry is lost

One of the monoclinic unit cell axes is unique since it is perpendicular to the other two. The unique axis is b.

Triclinic

Essential symmetry

$a \neq b \neq c$

none

$\alpha \neq \beta \neq \gamma \neq 90^{0}$

1.4 Lattice, Bravais lattice

It is useful to represent the manner of repetition of atoms, ions or molecules in a crystal by an array of points:

the array ≡ a lattice
the points ≡ lattice points

NaCl structure shown in Fig.1.8(a) is represented by an array of points in Fig.1.8(b)

each point represents one Na and one Cl
but the location of lattice point (at Na, Cl or in between) is irrelevant. A unit cell can have lattice points at some specific positions → Lattice Type.

Units cell: constructed by linking the lattice points

Lattice type

Primitive, P: lattice points only at the corners, Fig.1.8(b)
B

Centered– additional lattice points at the center, Fig.1.8(b)A

several types of centered lattice

F: face centered lattice, additional points in each face
C– extra lattice points are on the ab faces
Fig.1.9 A–extra lattice points are on the bc faces
→ side centered lattice
I: body centered lattice, an extra point at the body center

Example: a. Cu metal, a face centered cubic structure, *fcc*
b. α-iron (Fe), a body centered cubic structure, *bcc*
c. CsCl, Cs at corners and Cl at the body center, but it is primitive. For a body centered lattice, the atoms located at the corners must be identical to those at the body center.

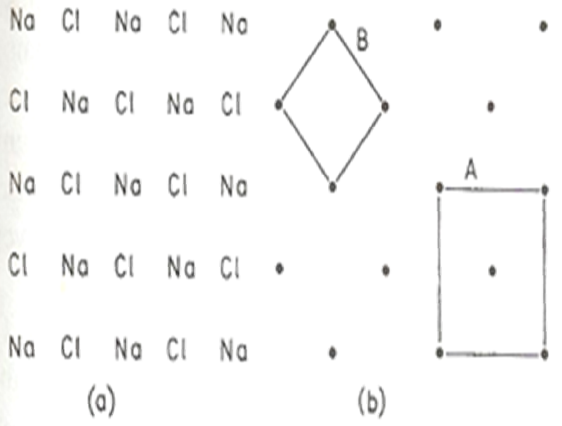


Fig. 1.8 Representation of (a) the NaCl structure in two dimensions by (b) an array of lattice points

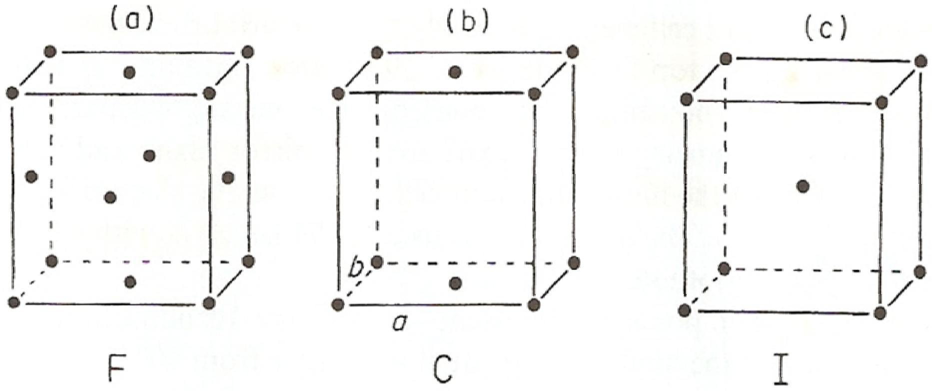


Fig. 1.9 (a) Face centred, (b) side centred and (c) body centred lattices

Combination of Crystal System and Lattice Type
→ fourteen Bravais lattices are possible

Table1.1 Crystal system (column 1); Lattice type (column 4)
e.g. primitive monoclinic, C–centered monoclinic, primitive triclinic

the trigonal lattice can be represented by a primitive rhombohedral lattice with a = b = c , $\alpha = \beta = \gamma \neq 90^{o}$ (Table 1.1 trigonal (b)), or a hexagonal lattice (stacking in ABCABC… sequence) of 3 lattice sites per cell (Hammond Fig. 3.3b, Table 1.1 trigonal (a), also belong to the hexagonal system)

Only 14 Bravais lattice are possible, and the reasons for absence
(a) violate symmetry requirements,
e.g. C–center lattice cannot be cubic (need threefold axes)
(b) can be represented by a smaller, alternative cell
e.g. a face centered tetragonal cell can be redrawn as a body centered tetragonal cell (the volume is halved, but the symmetry remains the same).

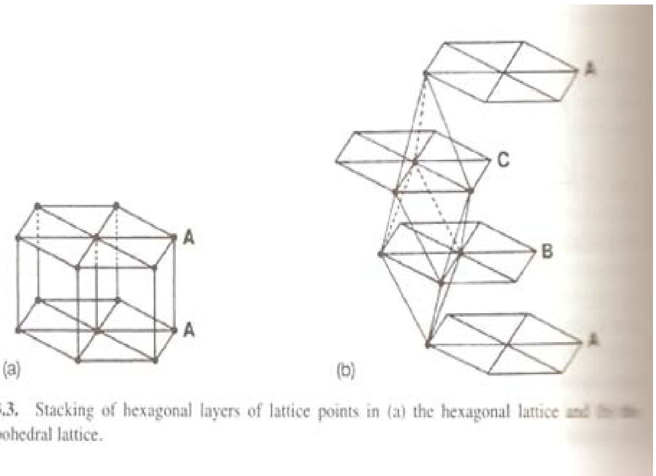


Fig. 3.3. Stacking of hexagonal layers of lattice points in (a) the hexagonal lattice and (b) the rhombohedral lattice.

Fig. 3.3a, hexagonal lattice: they are stacked directly one on top of the other.
Fig. 3.3b, rhombohedral lattice: the next two layers of point lie above the triangular “hollow” or interstices of the layer below, giving a three layer repeat.

1.5 Lattice planes and Miller indices

Lattice planes, a concept introduced with Bragg's law of diffraction, are defined from shape and dimensions of the unit cell.

Lattice planes are imaginary and provide a reference grid to which the atoms in the crystal structure may be referred.

Sometimes, a given set of lattice planes coincides with layers of atoms, but not usually.

Fig.1.10(a)

- 2D array of lattice points
- different sets of rows and for each there is a characteristic perpendicular distance, d , between adjacent rows.
- in 3D, rows → lattice planes interplanar d-spacing, d. The Bragg diffraction angle, θ, for each set is related to the d-spacing.

Lattice planes are labeled by assigning three numbers known as Miller indices to each set. Fig.1.10 (b)

Fig.1.10 (b) shows two planes are parallel and pass obliquely through the unit cell. A third plane in this set must, by definition, pass through the origin O. (many more parallel planes in this set)

To assign Miller indices to a set of planes, there are three stages:

1. Identify the plane which is adjacent to the one that passes through the origin
2. Find the interaction of this plane on the three axes:

   cuts x-axis at $\frac{a}{2}$, y-axis at b, z-axis at $\frac{c}{3}$.

   i.e. $(\frac{1}{2}, 1, \frac{1}{3})$ the fractional intersections

3. Take reciprocals of these fractions →(213)

   three integers, (213) are the Miller indices of the plane and all other planes that are parallel to it and are separated from adjacent planes by the same d-spacing.

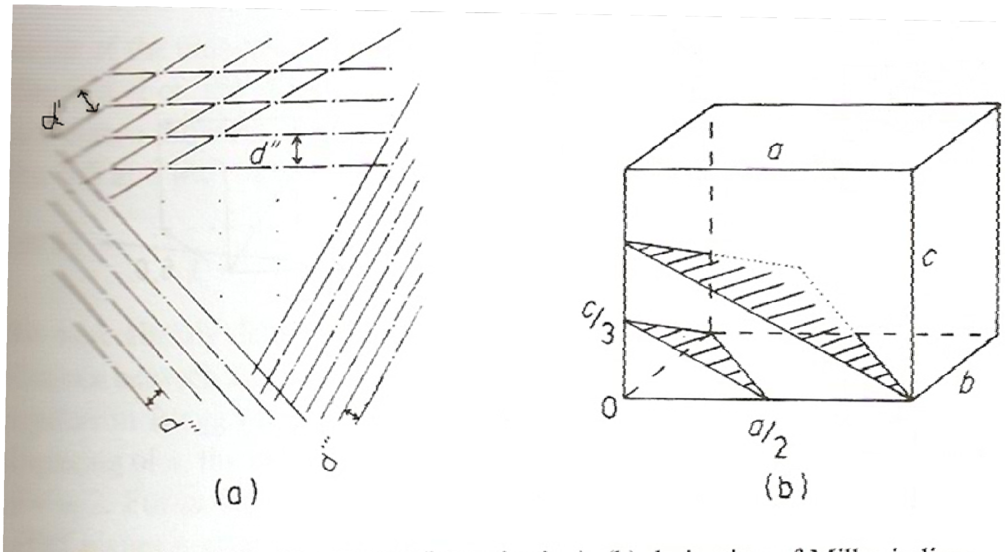


Fig. 1.10 (a) Lattice planes (in projection); (b) derivation of Miller indices

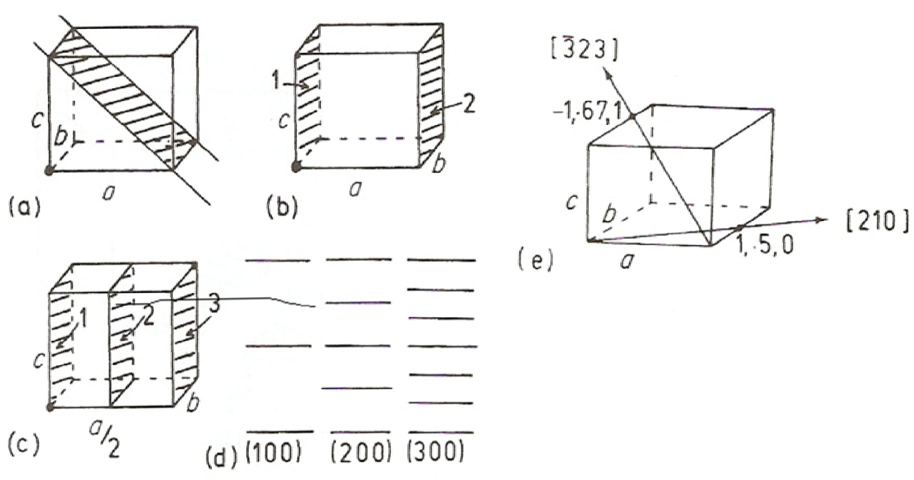


Fig. 1.11 Examples of Miller indices: (a) (101); (b) (100); (c) (200); (d) (h00); (e) indices of directions [210] and [$\bar{3}$23]

Some examples for determining the Miller indices

Fig. 1.11(a)

The shaded plane cuts x,y,z at 1a, ∞b, 1c

∴ Miller indices

The plane parallel to b

⇒ (101)

Plane is parallel to the axis with ”0”

Fig. 1.11(b)

Planes 1 and 2 comprise opposite faces of the unit cell

Plane 1 passes through the origin (cannot be used to determine indices)

Plane 2 has intercepts at 1a, ∞b, ∞c

⇒ (100) as the Miller indices

Fig. 1.11(c)

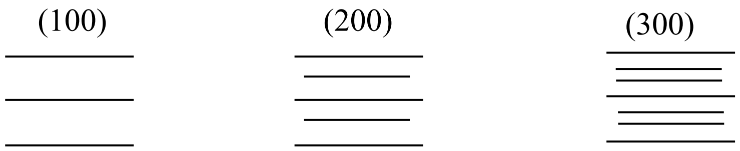
There are twice as many planes as in Fig. 1.11(b)

Plane 2 is the one that is closest to the origin

Intercepts at 1/2, ∞, ∞

(200) as the Miller index for all the planes, the (200) set.

Fig. 1.11 (d)



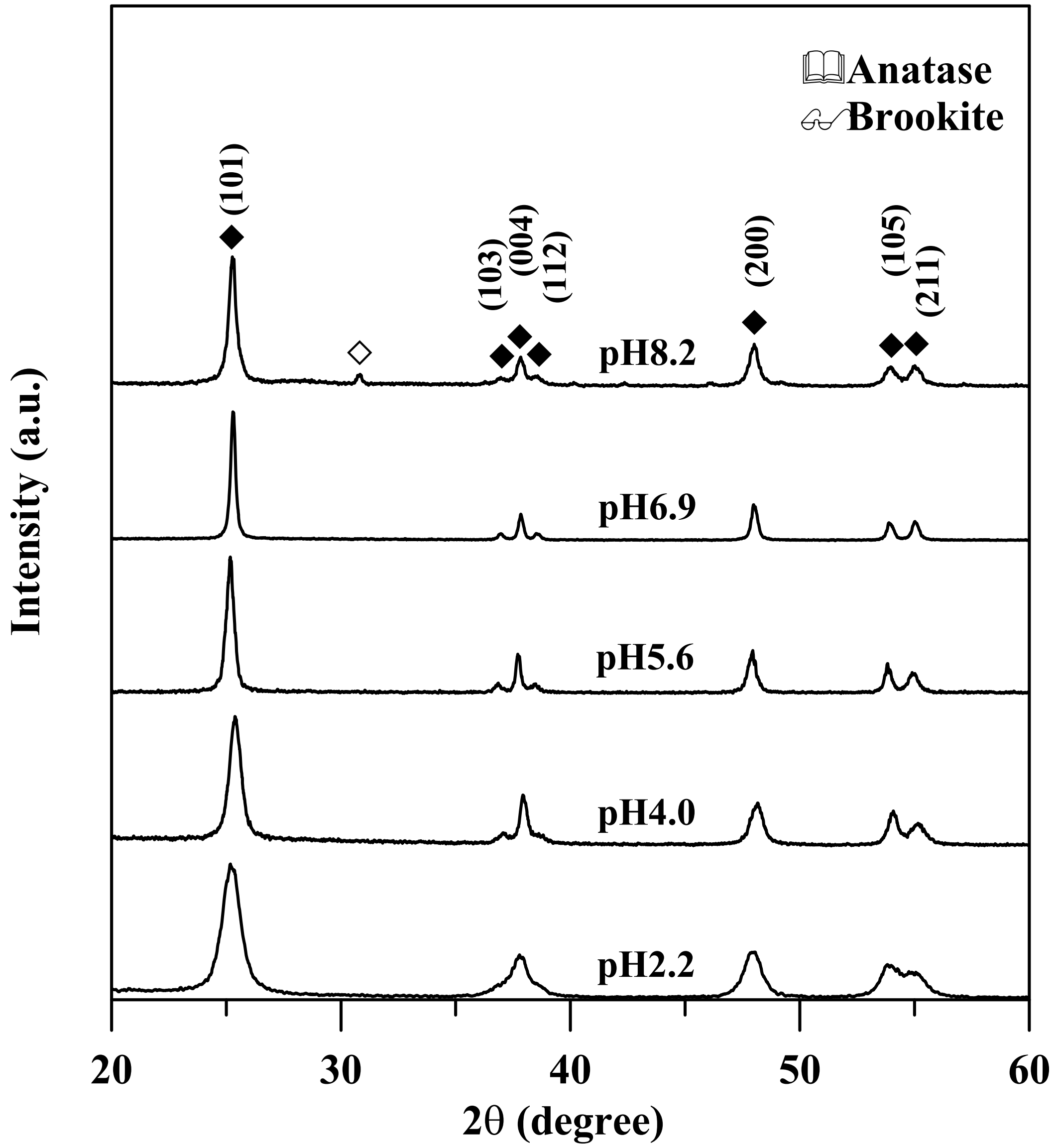
If extra planes are interleaved between adjacent (100) planes then all planes labeled as (200); likewise for (300).

General symbol for Miller indices in (hkl)

Symbol { } is used to indicate sets of planes that are equivalent,

e.g. the sets (100), (010) and (001) are equivalent in cubic crystals

⇒ represents collectively as {100}



High-resolution TEM image of a single TiO_2 nanorod obtained from hydrothermal treatment (at 175°C for 48 h) of a nanotube suspension with pH = 5.6 and the corresponding selected-area electron diffraction pattern (inset).

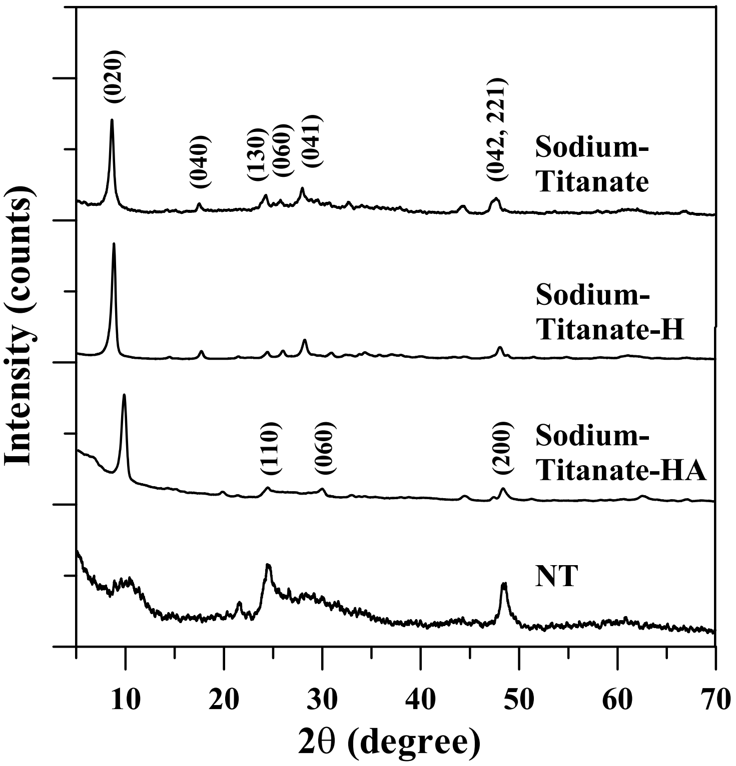


Figure 1. Powder XRD patterns of the titanate specimens obtained from the solid-state synthesis (designated as Sodium-Titanate), from the hydrothermal treatment on Sodium-Titanate (designated as Sodium-Titanate-H), and from the acid treatment on Sodium-Titanate-H to pH values of 6 and 1.7 (designated as Sodium-Titanate-HA and NT, respectively). The diffraction peaks are indexed according to the orthorhombic-phase structure shown in Figures 4a and b for Sodium-Titanate and Sodium-Titanate-HA, respectively.

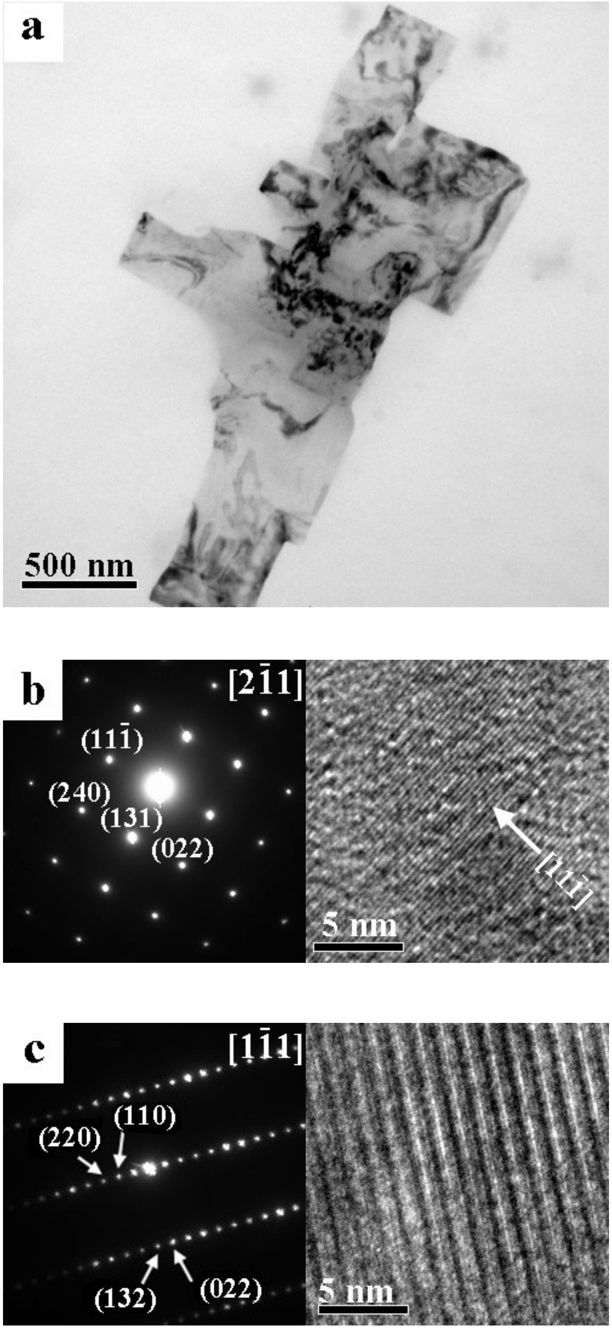


Figure 2 TEM images of the Sodium-Titanate specimen obtained from the solid-state synthesis (a) and the selected area electron diffraction patterns with their corresponding HRTEM images showing the lattice fringes directing along the zone axis $[2\ \bar{1}\ 1]$ (b) and the axis $[1\ \bar{1}\ 1]$ (c).

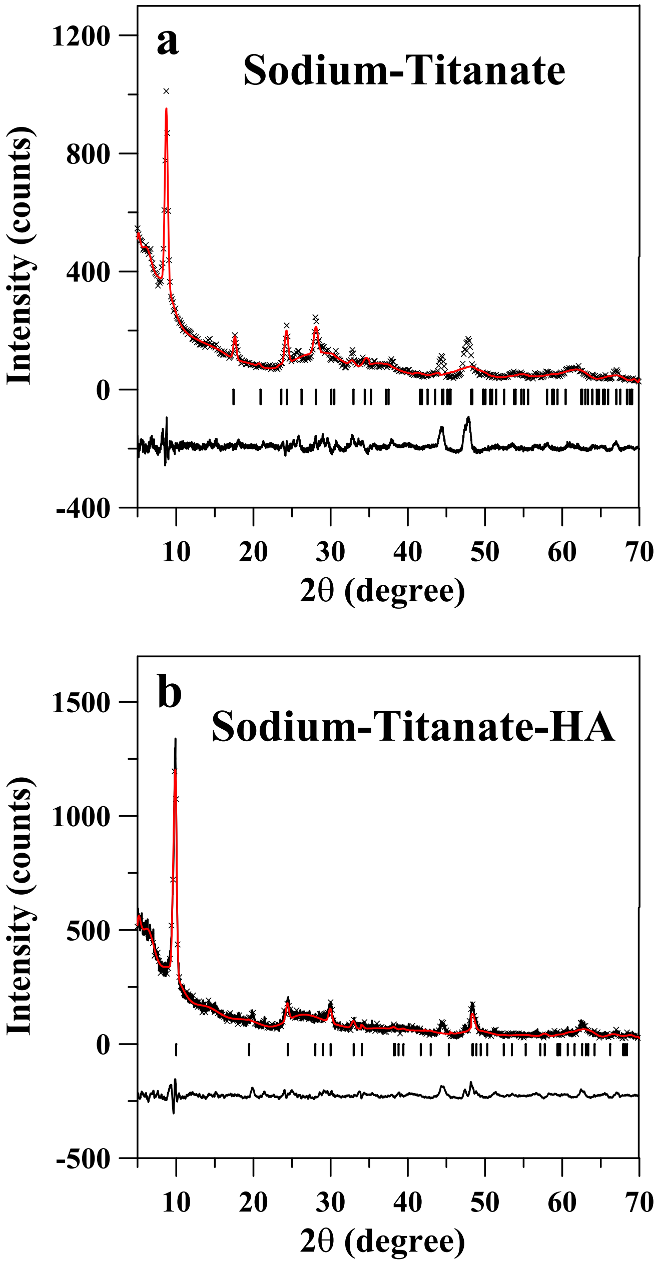


Figure 3 Observed (dot) and Rietveld-refinement simulated (line) XRD profiles for the Sodium-Titanate and Sodium-Titanate-HA specimens. The difference between the observed and simulated data is shown at the bottom of the figures. The reliability factors are $R_{wp} = 0.129$ and $R_p = 0.085$ for Sodium-Titanate and $R_{wp} = 0.123$ and $R_p = 0.087$ for Sodium-Titanate-HA.

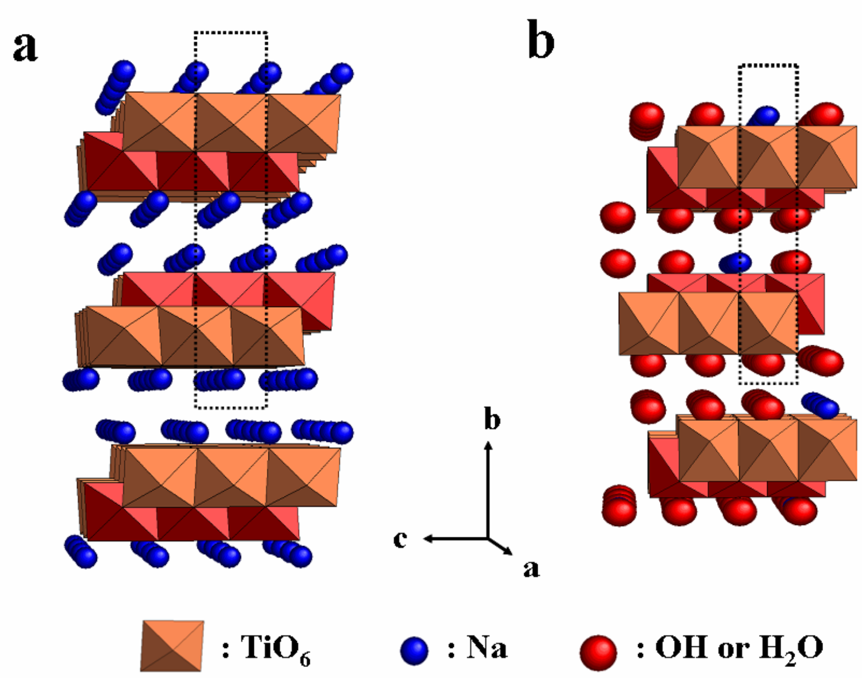
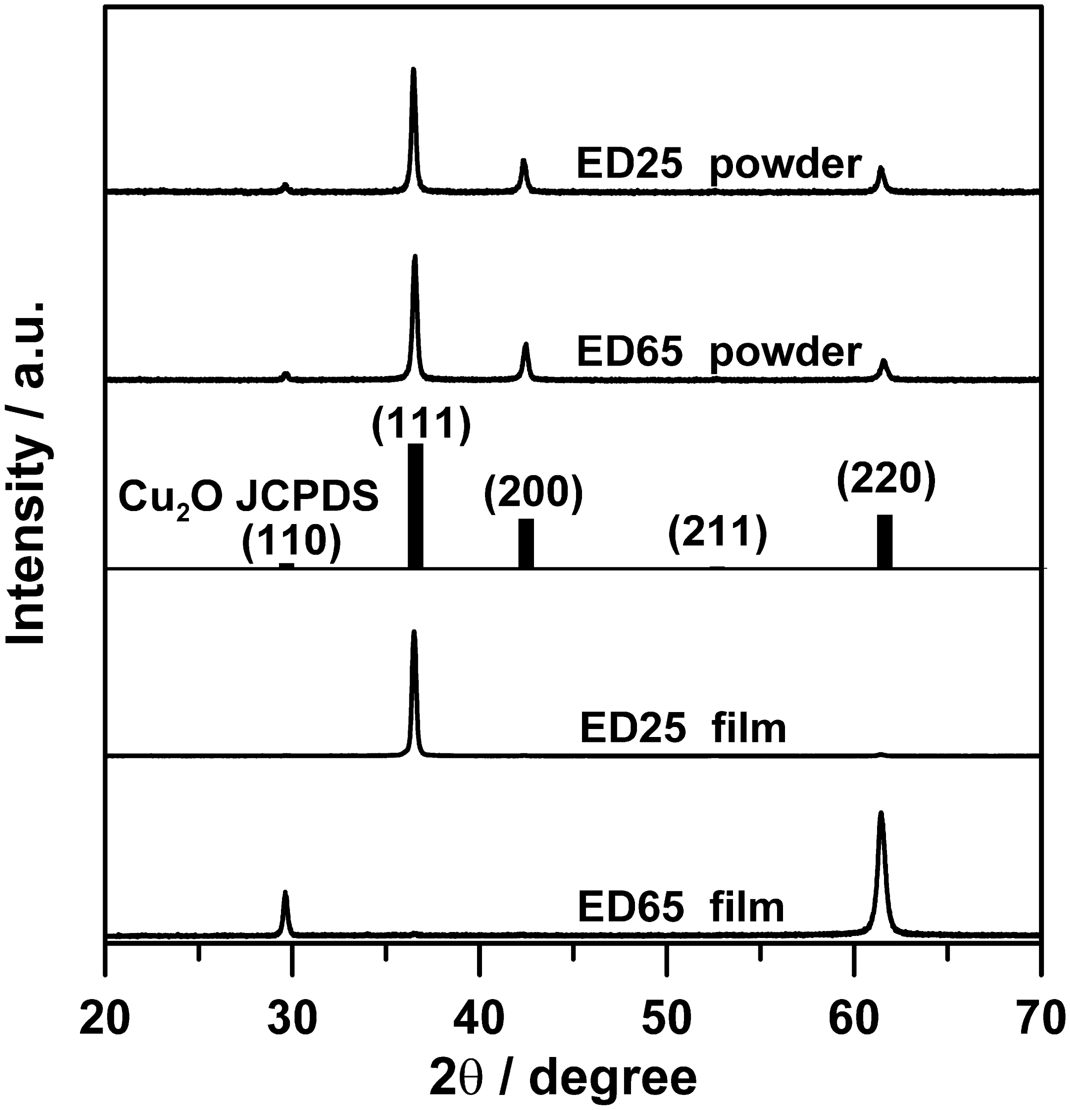


Figure 4 Proposed crystal structures of $Na_xTi_{2-x/4}\square_{x/4}O_4$ for the Sodium-Titanate specimen in orthorhombic C-base-centered symmetry (a) and $Na_{x+y-z}H_zTi_{2-x/4}\square_{x/4}O_4(OH)_y\cdot nH_2O$ for the Sodium-Titanate-HA specimen in orthorhombic body-centered symmetry (b). In both models the interlayer sites are shown in a fully occupied situation. Because of the small scattering factor for H atoms, OH and H_2O are not distinguished in the structural simulation. The change from the C-base-centered symmetry to the body-centered symmetry can be caused by a slip of the middle layer by $c_0/2$ along the c axis against the top and bottom layers.



Powder X-ray diffraction patterns of the ED25 and ED65 Cu_2O powders (upper section) and the films (lower section). The standard diffraction pattern of Cu_2O from JCPDS is provided at the middle of this figure.

1.6 Indices of directions

Directions in crystals and lattices are labeled by first drawing a line that passes through the origin and parallel the direction of concern.

$[\frac{1}{2}\,\frac{1}{2}\,0]$, [110], [330] all describe the same direction, but conventionally [110] is used. [xyz] are arranged to the set of smallest possible integers.

Cubic [100], [010], [001] are equivalent and can be represented collectively as <100>

For cubic systems, [hkl] directions is always perpendicular to the (hkl) plane of the same indices, but this is only sometimes true in non-cubic systems.

Fig. 1.11 (e), [210], $[\bar{3}23]$
[210]: taking the origin at the bottom left front corner
taking the intersection point: 1, 0.5, 0, to define the direction

$[\bar{3}23]$: taking the origin at the bottom right front corner
taking the intersection point: –1, 0.67, 1, to define the direction
the ***bar*** sign indicates a negative direction

1.7 d-spacing formulas

For a cubic unit cell,
The (100) planes have a d-spacing of a
The (200) planes, d = a/2

For orthorhombic crystals ($\alpha = \beta = \gamma = 90^{\circ}$)

$$\frac{1}{d_{hkl}{}^{2}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

for (hkl) planes this eq. can be used for:

tetragonal: $a = b \neq c$

cubic: $a = b = c$

For monoclinic and triclinic crystals
See Appendix 1

1.8 Crystal densities and unit cell contents

Formula weight

$$D = \frac{Mass}{Volume} = \frac{FW}{molar\ volume} = \frac{FW}{Volume\ of\ \ formula\ unit \times N}$$

N = Avogadro’s number

Z = content of formula unit in a unit cell
= unit cell content

V = unit cell volume
= volume of one formula unit × Z

On the basis of unit cell

$$\therefore \underset{\substack{\uparrow \\ \text{gcm}^{-3}}}{D} = \frac{FW \times Z}{\underset{\substack{\nwarrow \\ \times \frac{10^{-24} cm^3}{1\mathring{A}^3}}}{V} \times \underset{\substack{\nwarrow \\ 6.02 \times 10^{23}}}{N}} = \frac{FW \times Z \times 1.66}{\underset{\substack{\leftarrow \\ \mathring{A}^3}}{V}}$$

Uses of the above equation:

a. to check that a given set of crystal data is consistent and that an erroneous formula weight has not been assumed.

b. to determine any of the four variables if the other three are known.

c. by comparison of D_{obs} and D_{calc}, information may be obtained on the presence of crystal defects such as vacancies or interstitials, the mechanisms of solid solution formation and the porosity of ceramic pieces.

Z value determination

Fig. 1.9(c), α-Fe, body-centered cubic (*bcc*)

The corner atoms: 8, each is shared between eight neighboring unit cells
The body center atom: 1, entirely inside the unit cell

$$Z = (8 \times \frac{1}{8}) + 1 = 2$$

Fig. 1.9(a), face-centered cubic (*fcc*), Cu

The corner atoms: 8
The face center atoms: 6, each shared between two unit cells

$$Z = (8 \times \frac{1}{8}) + (6 \times \frac{1}{2}) = 4$$

Fig. 1.2, NaCl, *fcc*

Assuming the origin at Na $\rightarrow$ same as Cu

$\therefore$unit cell contains 4 Na

Cl: edge center positions: 12, each shared between four

body center: 1

$\therefore$unit cell contains 4 Cl $= (12 \times \frac{1}{4}) + 1$

Z = 4 NaCl

Appendix 1

Interplanar Spacings and Unit Cell Volumes

The value of d, the perpendicular distance between adjacent planes in the set (hkl), may be calculated using the formulae:

Cubic	$\frac{1}{d^2}=\frac{h^2+k^2+l^2}{a^2}$
Tetragonal	$\frac{1}{d^2}=\frac{h^2+k^2}{a^2}+\frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{h^2}{b^2}+\frac{l^2}{c^2}$
Hexagonal	$\frac{1}{d^2}=\frac{4}{3}\left(\frac{h^2+hk+k^2}{a^2}\right)+\frac{l^2}{c^2}$
Monoclinic	$\frac{1}{d^2}=\frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2}+\frac{k^2\sin^2\beta}{b^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}\right)$
Triclinic	$\frac{1}{d^2}=\frac{1}{V^2}[h^2b^2c^2\sin^2\alpha+k^2a^2c^2\sin^2\beta$ $+l^2a^2b^2\sin^2\gamma+2hkabc^2(\cos\alpha\cos\beta-\cos\gamma)$ $+2kla^2bc(\cos\beta\cos\gamma-\cos\alpha)$ $+2hlab^2c(\cos\alpha\cos\gamma-\cos\beta)]$

where V is the cell volume. The unit cell volumes are given by:

Cubic	$V=a^3$
Tetragonal	$V=a^2c$
Orthorhombic	$V=abc$
Hexagonal	$V=(\sqrt{3}a^2c)/2=0.866a^2c$
Monoclinic	$V=abc\sin\beta$
Triclinic	$V=abc(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{1/2}$