f) Rutile (TiO_2), cadmium iodide (CdI_2), cadmium chloride ($CdCl_2$) and caesium oxide (Cs_2O)

Together with fluorite, they represent the main AX_2 structure types.

Rutile TiO_2– tetragonal unit cell with a = b = 4.594 Å, c = 2.958 Å
Fig. 1.32a: Ti positions, 2 per cell, corner(0,0,0) and body center($\frac{1}{2},\frac{1}{2},\frac{1}{2}$)
O positions, (x,x,0); (1-x, 1-x,0); ($\frac{1}{2}$+x,$\frac{1}{2}$-x,$\frac{1}{2}$);($\frac{1}{2}$-x,$\frac{1}{2}$+x, $\frac{1}{2}$). x value must be determined experimentally (x ~ 0.3).

Fig. 1.32b: Ti($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) is coordinated octahedrally to 6 oxygens. Four of them are coplanar with Ti– two at z = 0and two at 1 (directly above the two at z=0). The other two of them (at z =$\frac{1}{2}$) are collinear with Ti and form the axes of octahedron. The corner Ti also octahedrally coordinated but with different orientations.

The oxygens are coordinated trigonally to 3 Ti: oxygen 0 in Fig. 1.32a is coordinated to Ti at the corner, the body center and the body center of the cell below.

Fig. 1.32c: TiO_6 octahedra link by sharing edges and corners to form a 3D framework. Consider the TiO_6 in the center of the cell in Fig. 1.32b; similar octahedra in identical orientation occur above and below by sharing edges to form infinite chains parallel to *c*. These chains are similarly formed by TiO_6 centered at the corners. The two types of chains link by their corners to form a 3D framework; they differ about z by 90° and are c/2 out of step with each other.

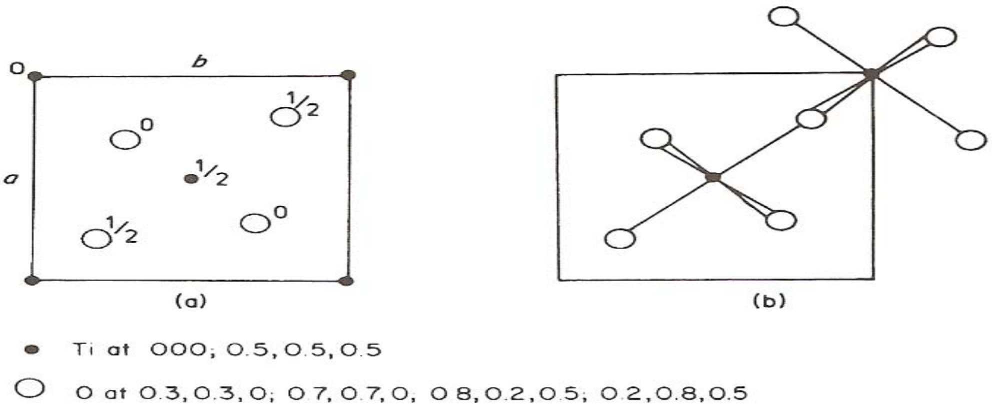
Fig. 1.32d,e: Rutile is commonly described as a distorted hcp oxide array with half the octahedral sites occupied by Ti. (d) corrugated oxide cp layers occur horizontally and vertically; (e) undistorted hcp arrangement, in which cp layers occurs only horizontally.

Fig. 1.33: (a) two ideal hcp layers. While all octahedral sites are occupied

in NiAs, alternate horizontal rows are full and empty (dash line shows the rutile unit cell). (b) Parallel to the tetragonal c axis, the TiO_6 octahedra share edges (oxygens 1 and 2 forming the common edge).

The bond lengths of Ti–O
Ti($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and O(0.3,0.3,0): ($\frac{1}{2}$–0.3)a = 0.92Å, ($\frac{1}{2}$–0)c = 1.48Å; ∴ Ti–O = $\sqrt{0.92^2+0.92^2+1.48^2}$ Å = 1.97Å
Ti($\frac{1}{2},\frac{1}{2},\frac{1}{2}$) and O (0.8,0.2,$\frac{1}{2}$): Ti–O = $\sqrt{(0.3a)^2+(0.3a)^2}$ = 1.95Å

Table 1.15 compounds of rutile structure
*Oxides of tetravalent metals and fluorides of divalent metals
*The metals are too small to have 8-coordination as in the fluorite structure.



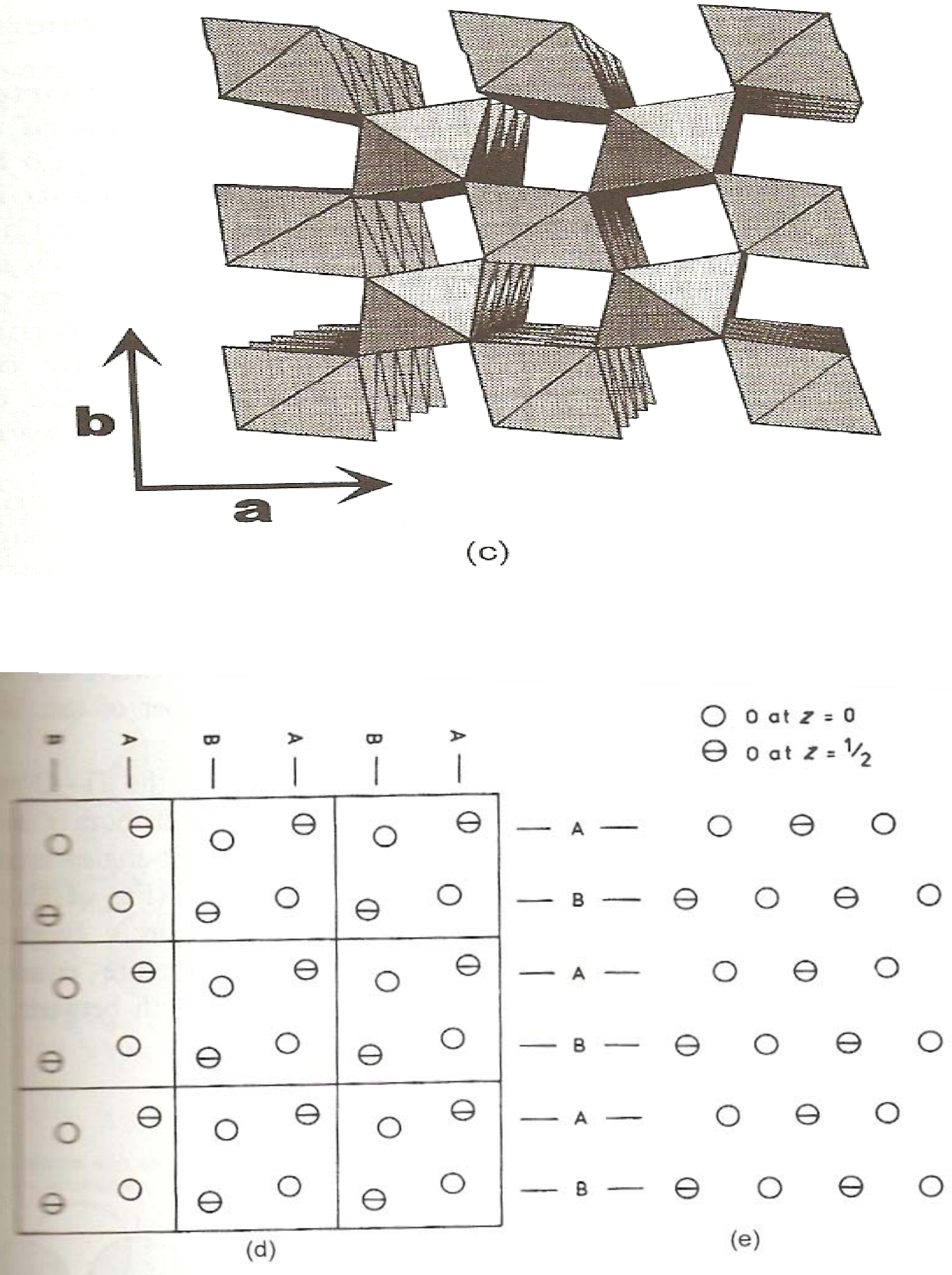


Fig. 1.32 The rutile structure, TiO_2

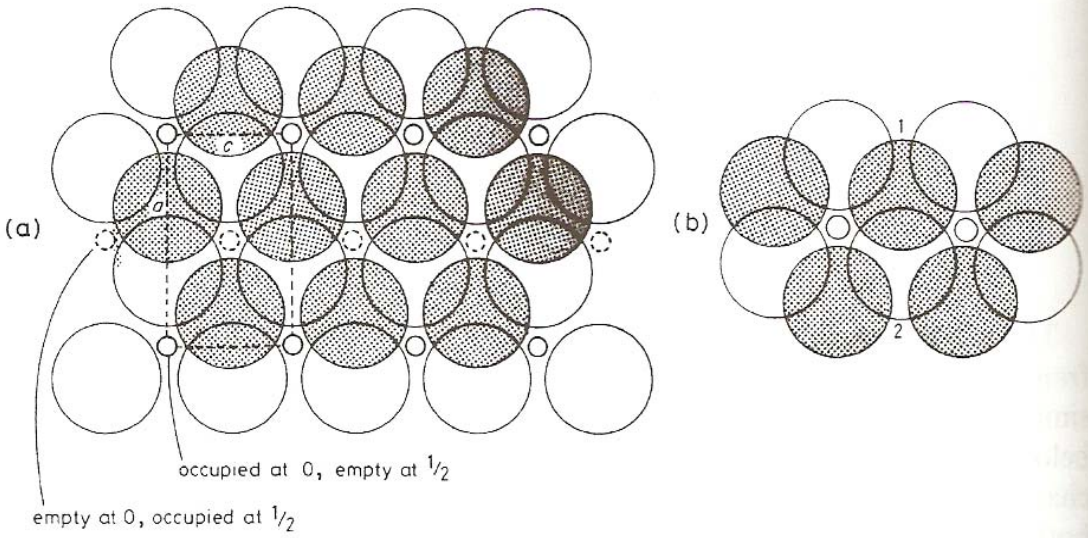


Fig. 1.33 The rutile structure: (a) in idealized form, with planar oxide layers; (b) edge-sharing octahedra forming horizontal rows

Table 1.15 *Some compounds with the rutile structure* (Wyckoff, 1971, Vol. 1)

	a(Å)	*c*(Å)	*x*		*a*(Å)	*c*(Å)	*x*
TiO_2	4.5937	2.9581	0.305	CoF_2	4.6951	3.1796	0.306
CrO_2	4.41	2.91		FeF_2	4.6966	3.3091	0.300
GeO_2	4.395	2.859	0.307	MgF_2	4.623	3.052	0.303
IrO_2	4.49	3.14		MnF_2	4.8734	3.3099	0.305
β-MnO_2	4.396	2.871	0.302	NiF_2	4.6506	3.0836	0.302
MoO_2	4.86	2.79		PdF_2	4.931	3.367	
NbO_2	4.77	2.96		ZnF_2	4.7034	3.1335	0.303
OsO_2	4.51	3.19		SnO_2	4.7373	3.1864	0.307
PbO_2	4.946	3.379		TaO_2	4.709	3.065	
RuO_2	4.51	3.11		WO_2	4.86	2.77	

CdI_2– nominally very similar to rutile, because it also has an hcp anion array with half the octahedral sites occupied by M^{2+}. However, the manner of occupancy is quite different.

Fig. 1.34. The entire layers of octahedral sites are occupied and alternate with layers of empty sites. CdI_2 is therefore a layered material (in both the crystal structure and properties).
(a) Two I layers in a hcp array with the octahedral sites in between occupied by Cd.
(b) The layer stacking sequence along *c*. I layers form an …ABAB… stacking. Cd may be regarded as the C positions. A sandwich structure in which Cd^{2+} ions are sandwiched between layers of I^- and adjacent sandwiches are held together by weak van der Waals bonds. CdI_2 may be regarded as an infinite sandwich 'molecule' in which Cd–I is strong but bonds between adjacent molecules are weak.
(c) coordination of I in CdI_2. An I at $c = \frac{1}{4}$ has <u>three</u> close Cd neighbors to one side at c = 0. The next nearest neighbors are twelve I (the hcp array).
(d) CdI_6 octahedra link by sharing edges to form infinite sheets. No direct linkages between adjacent sheets to support 3D model.

Table 1.16 some compounds having the CdI_2 structure
Mainly in transition metal iodides, bromides, chlorides and hydroxides.
TiS_2 was a potential intercalation host cathode for lithium ion batteries.
Li^+ is able to diffuse into the empty layers and electrons can enter and migrate through the 3d orbital on Ti.

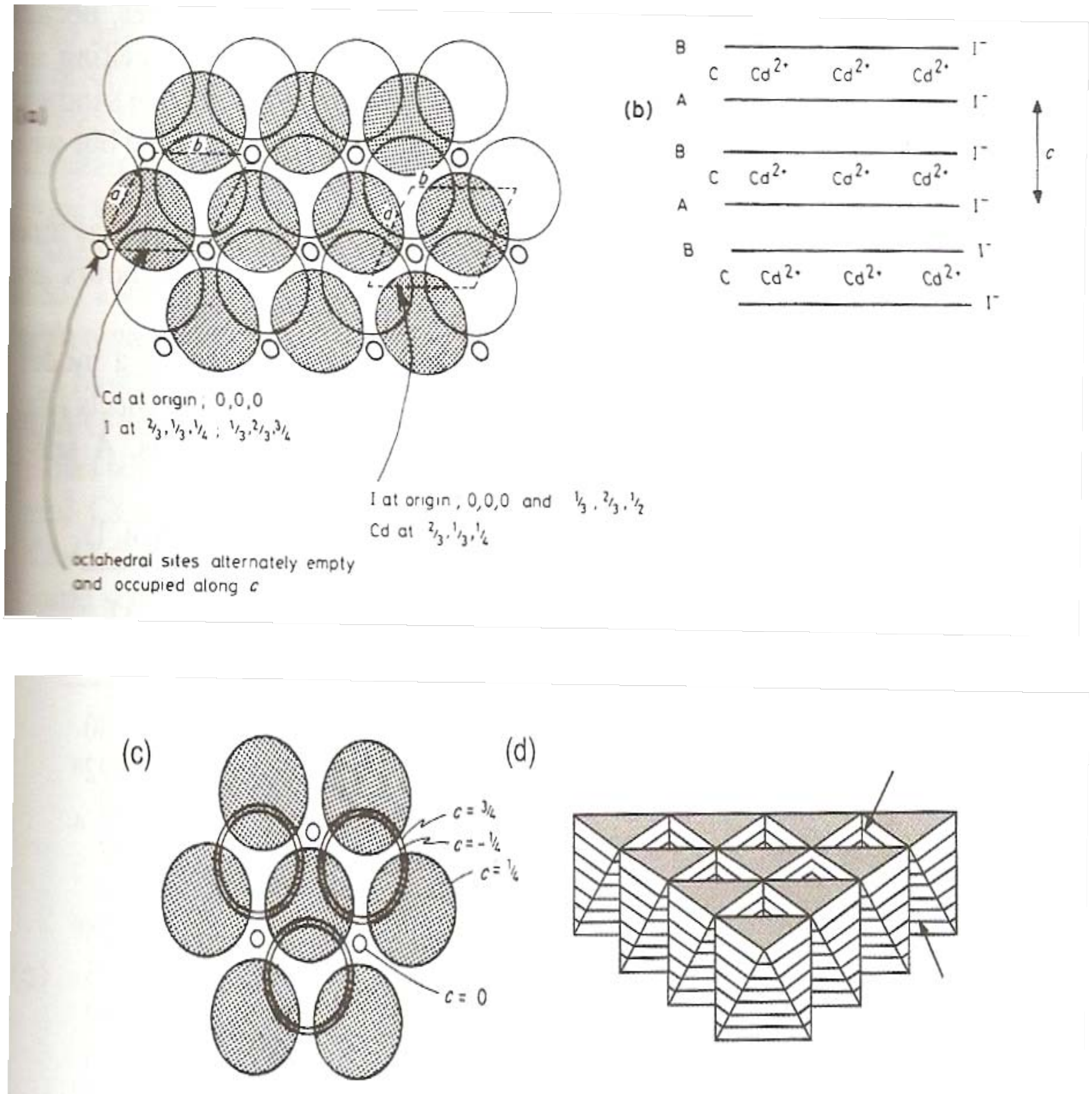


Fig. 1.34 The CdI_2 structure: (a) the basal plane of the hexagonal unit cell, with two possible choices of origin; (b) the layer stacking sequence; (c) the coordination environment of I; (d) a layer of close packed octahedra

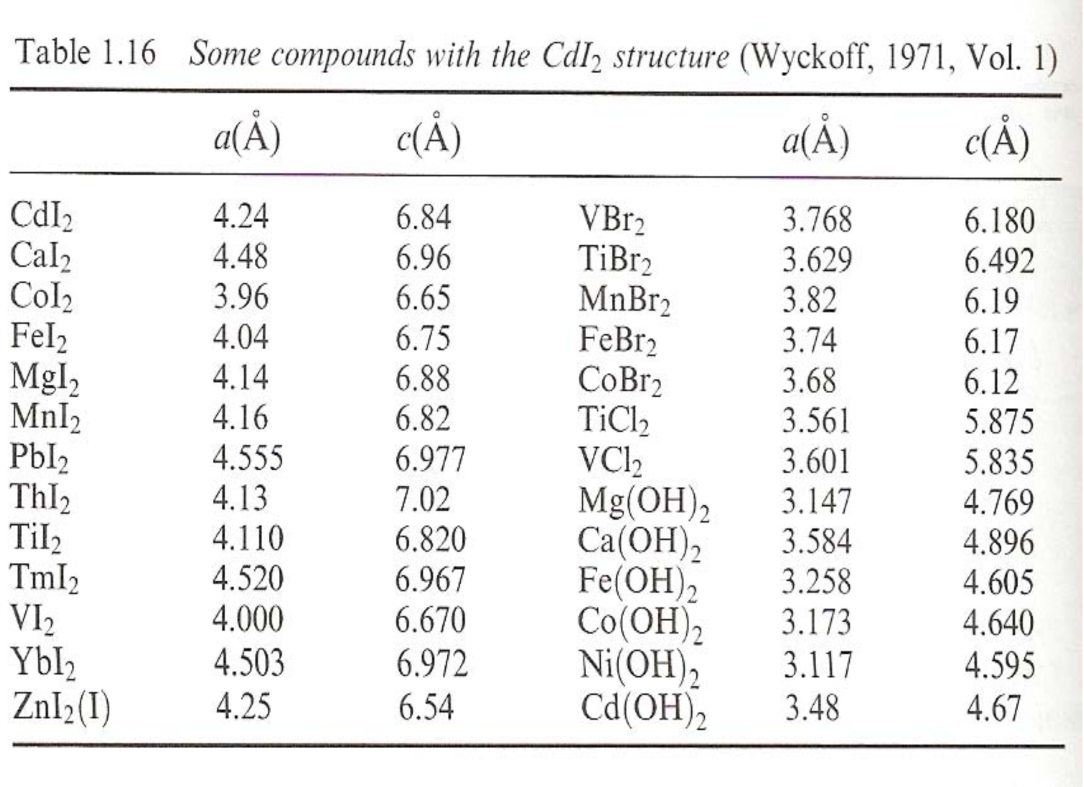


Table 1.16 *Some compounds with the CdI_2 structure* (Wyckoff, 1971, Vol. 1)

	a(Å)	c(Å)		a(Å)	c(Å)
CdI_2	4.24	6.84	VBr_2	3.768	6.180
CaI_2	4.48	6.96	$TiBr_2$	3.629	6.492
CoI_2	3.96	6.65	$MnBr_2$	3.82	6.19
FeI_2	4.04	6.75	$FeBr_2$	3.74	6.17
MgI_2	4.14	6.88	$CoBr_2$	3.68	6.12
MnI_2	4.16	6.82	$TiCl_2$	3.561	5.875
PbI_2	4.555	6.977	VCl_2	3.601	5.835
ThI_2	4.13	7.02	$Mg(OH)_2$	3.147	4.769
TiI_2	4.110	6.820	$Ca(OH)_2$	3.584	4.896
TmI_2	4.520	6.967	$Fe(OH)_2$	3.258	4.605
VI_2	4.000	6.670	$Co(OH)_2$	3.173	4.640
YbI_2	4.503	6.972	$Ni(OH)_2$	3.117	4.595
ZnI_2(I)	4.25	6.54	$Cd(OH)_2$	3.48	4.67

$CdCl_2$– closely related to $CdCl_2$ structure and different in the nature of anion packing; Cl^- ions are *ccp* in $CdCl_2$ whereas I is *hcp* in $CdCl_2$.

Fig. 1.35. (a) $CdCl_2$ may be represented by a hexagonal unit cell. The base is of similar size and shape to that in $CdCl_2$ but its c axis is three times as long as c in CdI_2. This is because in $CdCl_2$, the Cd positions are staggered along c and give rise to a three-layer repeat for Cd and six-layer repeat for Cl. In CdI_2 the Cd positions are stacked on top of each other and the c repeat contains only two I layers and one Cd layer.

(b) $CdCl_2$ in projection down c. (a) Cl layers occur at c = 0(A), $\frac{2}{12}$(B), $\frac{4}{12}$(C) and sequence is repeated at c = $\frac{6}{12}, \frac{8}{12}, \frac{10}{12}$. Cd occupies octahedral sites at c = $\frac{1}{12}, \frac{5}{12}, \frac{9}{12}$. The octahedral sites at c = $\frac{3}{12}$ are empty and directly below Cd at $\frac{9}{12}$.

Table 1.17 (some compounds with the $CdCl_2$ structure). They occur with a variety of transition metal halides. They are layered and have bonding similar to that in CdI_2.

The structure of Cs_2O is anti-$CdCl_2$. Cs forms ccp layers and O occupies the octahedral sites between alternate pairs of Cs layers.

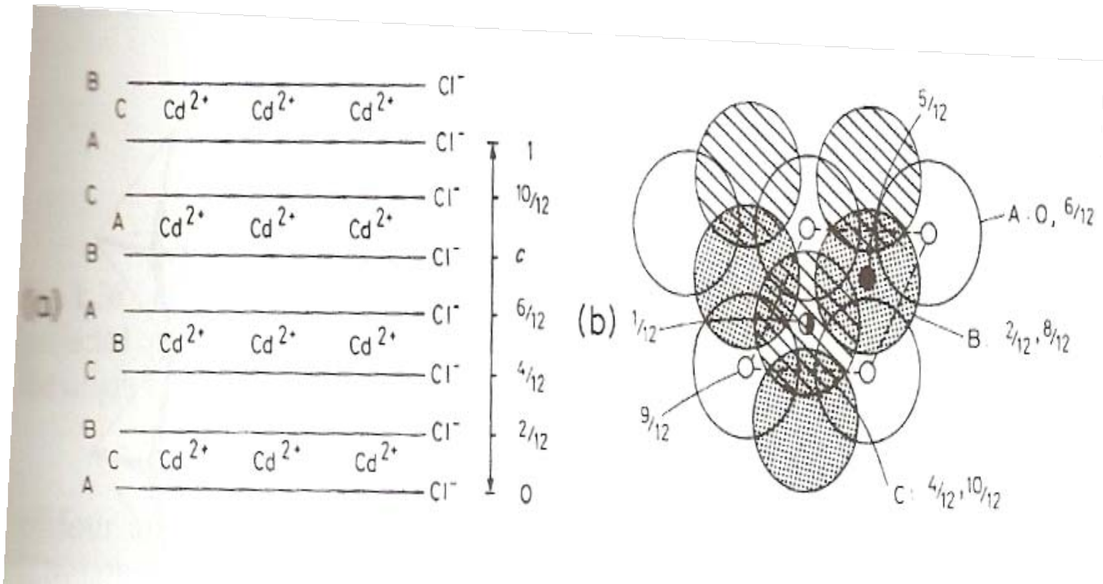


Fig. 1.35 The $CdCl_2$ structure

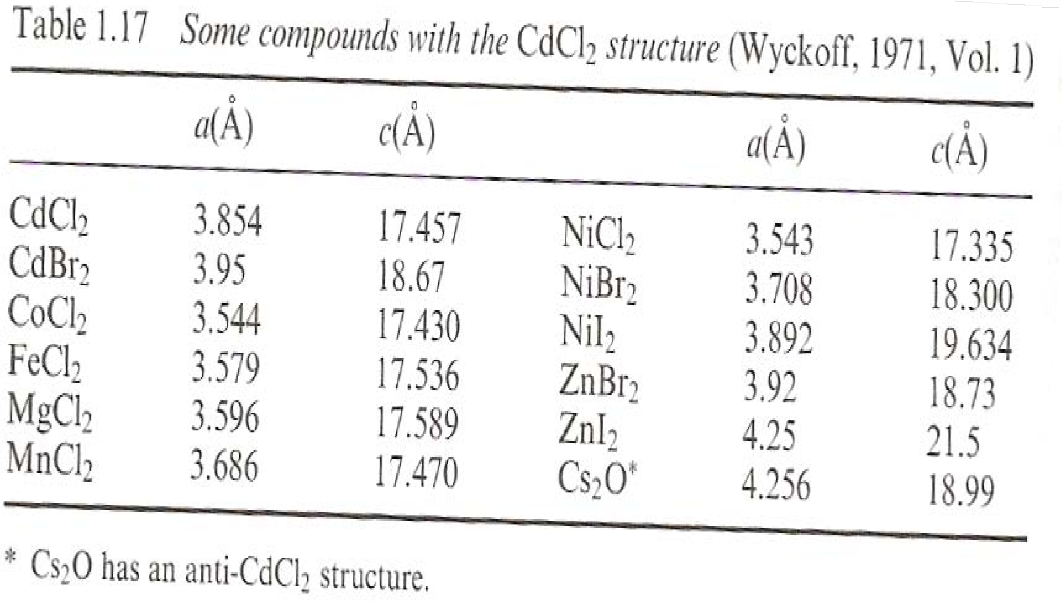


Table 1.17 *Some compounds with the* $CdCl_2$ *structure* (Wyckoff, 1971, Vol. 1)

	a(Å)	c(Å)		a(Å)	c(Å)
$CdCl_2$	3.854	17.457	$NiCl_2$	3.543	17.335
$CdBr_2$	3.95	18.67	$NiBr_2$	3.708	18.300
$CoCl_2$	3.544	17.430	NiI_2	3.892	19.634
$FeCl_2$	3.579	17.536	$ZnBr_2$	3.92	18.73
$MgCl_2$	3.596	17.589	ZnI_2	4.25	21.5
$MnCl_2$	3.686	17.470	Cs_2O*	4.256	18.99

* Cs_2O has an anti-$CdCl_2$ structure.

g) Perovskite ($SrTiO_3$)

This very important structure type (of general formula ABX_3) has a cubic unit cell shown as a projection down one axis (Fig. 1.36a) and as an oblique projection (b). It contains Ti at the cube corners (0,0,0), Sr at the body center ($\frac{1}{2},\frac{1}{2},\frac{1}{2}$), and O at edge centers ($\frac{1}{2}$,0,0; 0,$\frac{1}{2}$,0; 0,0,$\frac{1}{2}$).

Interatomic distances (Fig. 1.36b): Ti–O = a/2 = 1.953 Å; Sr is equidistant from all 12 oxygens at edge center positions. Sr–O = $\frac{1}{2}$(face diagonal) = $\sqrt{2}$ a/2 = 2.76Å

Coordination of O: Two nearest neighbors Ti at 1.953Å (linear), four Sr at 2.76Å, and eight other O at 2.76Å. Sr–O = O–O.

Perovskite does not contain cp oxide ions but O and Sr together do form a ccp array with the layers parallel to the {111}. To see this compare to the structure of NaCl (Fig. 1.2). The Cl at edge center and body center positions is in ccp, while in perovskite O at edge centers and Sr at body center. ∴ mixed Sr/O forms cp layers with $\frac{1}{4}$ of atoms are Sr.
Na in NaCl occupies all the octahedral sites (corners and face centers) while Ti occupies $\frac{1}{4}$ the octahedral sites (the corner sites).

Large cations, such as Sr^{2+} (r = 1.1Å), commonly play different roles in different structures: twelve coordinate packing ions in $SrTiO_3$ or octahedrally coordinated cations within a cp oxide array, SrO (rock salt).

3D framework: corner-sharing TiO_6 octahedra with Sr in 12-coordinate interstices. Each O is shared by two octahedra such that Ti–O–Ti is linear. Octahedra link at their corners to form sheets (Fig. 1.36d).

Table 1.18 (some perovskite compounds). Several hundred oxides and halides form perovskite structure. ABO_3: cations A and B have combined oxidation state of six. +I, +V as in $KNbO_3$; +II, +IV as in $CaTiO_3$; +III, +III as in $LaGaO_3$. The 12-coordinate A site cations are much larger than the 6-coordinate B site cations.

Some deviations:
*A variety of distorted, non-cubic structures exist for perovskite. These structures often form on cooling the high-temperature cubic structures and the framework of octahedra may be slightly twisted or distorted. Some have interesting and useful properties, such as ferroelectricity (Chap. 7).
*Two different cations may occupy either the A or B sites to form more complex perovskite.

i) Tolerance factor
In an ideal, cubic perovskite structure,

$$a = \sqrt{2}\, r_{A\text{–}O} = 2r_{B\text{–}O}$$

This equation tells how well the sizes of A and B atoms meet the requirement of an ideal perovskite. A tolerance factor, t, shows the degree of deviation: $t = \sqrt{2}\, r_{A\text{–}O}/2r_{B\text{–}O}$. In practice, a cubic perovskite forms with $0.9 < t < 1.0$.

For $t > 1$, the B site is larger than required (i.e. the B ion is too small). If t is slightly greater, the structure distorts but is still a perovskite as in $BaTiO_3$, $t = 1.06$. For larger departures from $t = 1.0$, the B ions demands a smaller site (of lower CN) and the structure changes completely, as in $BaSiO_3$ which has tetrahedral Si.

For $0.85 < t < 0.9$, a different structure distortion occurs (as in $GdFeO_3$) because the A cation is too small for its site.

For $t < 0.85$, distorted perovskite structures are no longer stable and the A cation requires a smaller site. E.g., $LiNbO_3$ and $FeTiO_3$, their structures are quite different from perovskite and their cations are all in octahedral sites.

ii) $BaTiO_3$

Fig. 1.36e (projection on ac plane of $BaTiO_3$). Tetragonal with a = 3.995, c = 4.034 Å. Since Ti is too small for its octahedral site, it displaces by about 6% of Ti–O towards one of the oxygens; Ba^{2+} also displace slightly in the same direction. This reduces the CN of Ti to 5 (square pyramidal) and the structure also contracts in the ab plane.

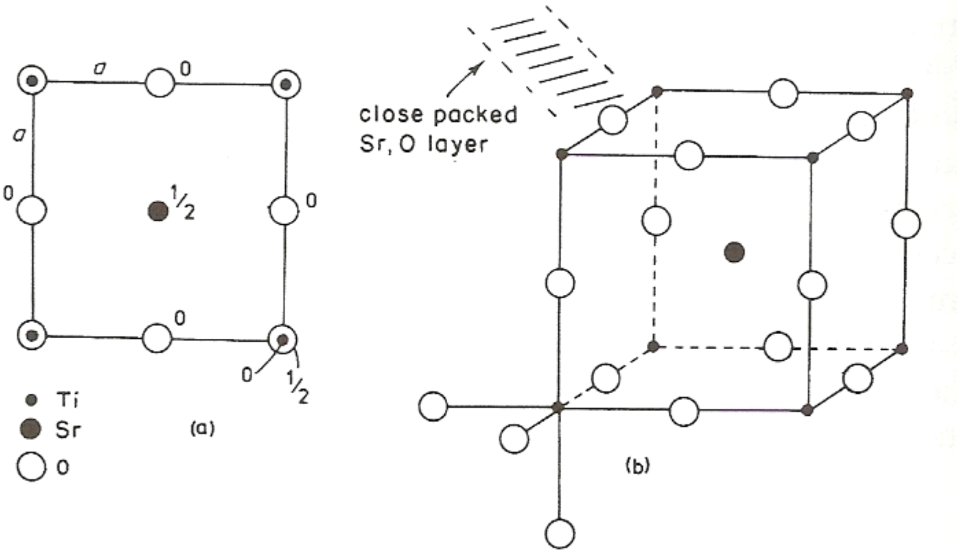
Because of the displacement of Ti atoms, the resulting structure has a large dipole moment. It is possible to flip the orientation of the dipole: under an applied electric field, the Ti atoms move through the center of the octahedral site towards one of the other corner oxygens. This ready reversibility is responsible for the property of ferroelectricity.

iii) $GdFeO_3$

Fig. 1.36f (the BO_6 octahedra are tilted in an alternating, zig-zag fashion. This reduce the size of A site and the CN from 12 to 8.

iV) Stoichiometry- property relations

Two different-sized cations, several possible cation charge combinations, and cation or anion vacancies → a very wide range of compositions and properties. Table 1.18b: perovskite-related structure.



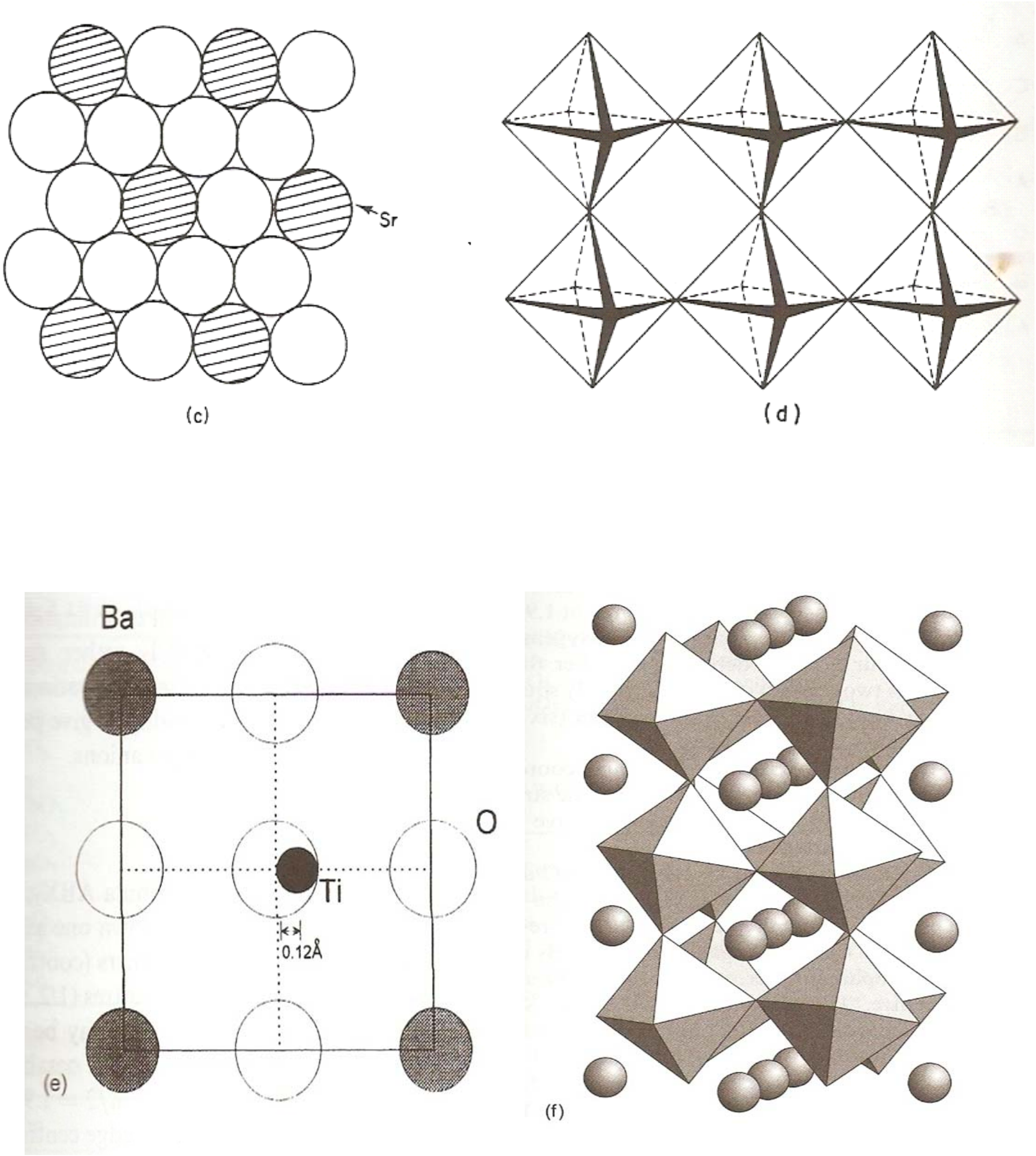


Fig. 1.36 (a–d) The perovskite structure of $SrTiO_3$. (e) Structure of tetragonal $BaTiO_3$ projected onto the *ac* plane. (From Weller, *Inorganic Materials Chemistry*, 1994.) Note, the origin of the unit cell is shifted to coincide with Ba rather than with Ti as in (a). (f) $GdFeO_3$ structure

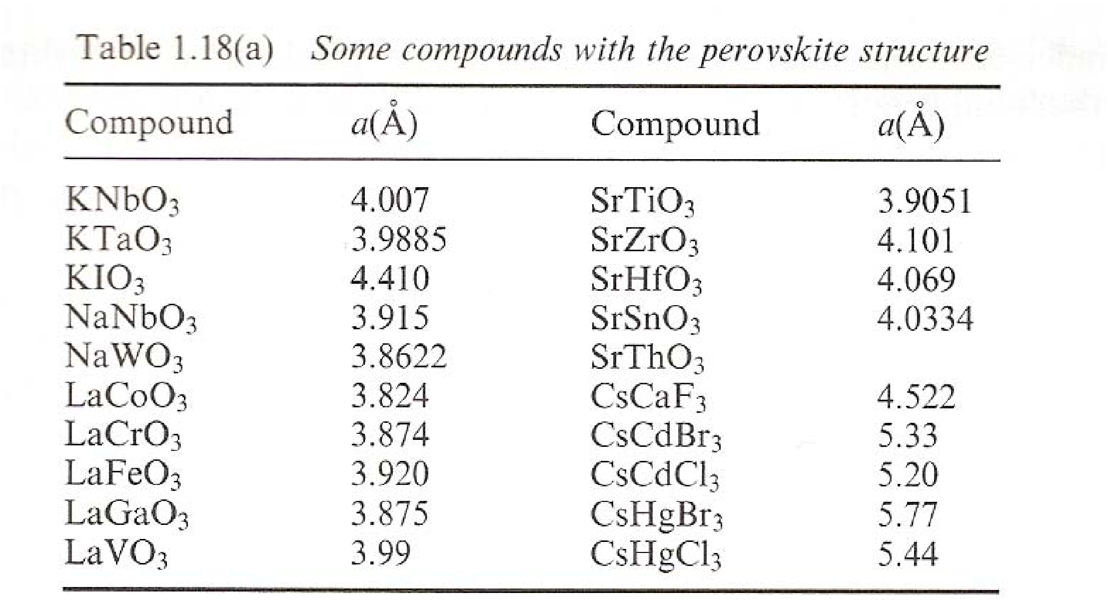


Table 1.18(a) *Some compounds with the perovskite structure*

Compound	a(Å)	Compound	a(Å)
$KNbO_3$	4.007	$SrTiO_3$	3.9051
$KTaO_3$	3.9885	$SrZrO_3$	4.101
KIO_3	4.410	$SrHfO_3$	4.069
$NaNbO_3$	3.915	$SrSnO_3$	4.0334
$NaWO_3$	3.8622	$SrThO_3$	
$LaCoO_3$	3.824	$CsCaF_3$	4.522
$LaCrO_3$	3.874	$CsCdBr_3$	5.33
$LaFeO_3$	3.920	$CsCdCl_3$	5.20
$LaGaO_3$	3.875	$CsHgBr_3$	5.77
$LaVO_3$	3.99	$CsHgCl_3$	5.44

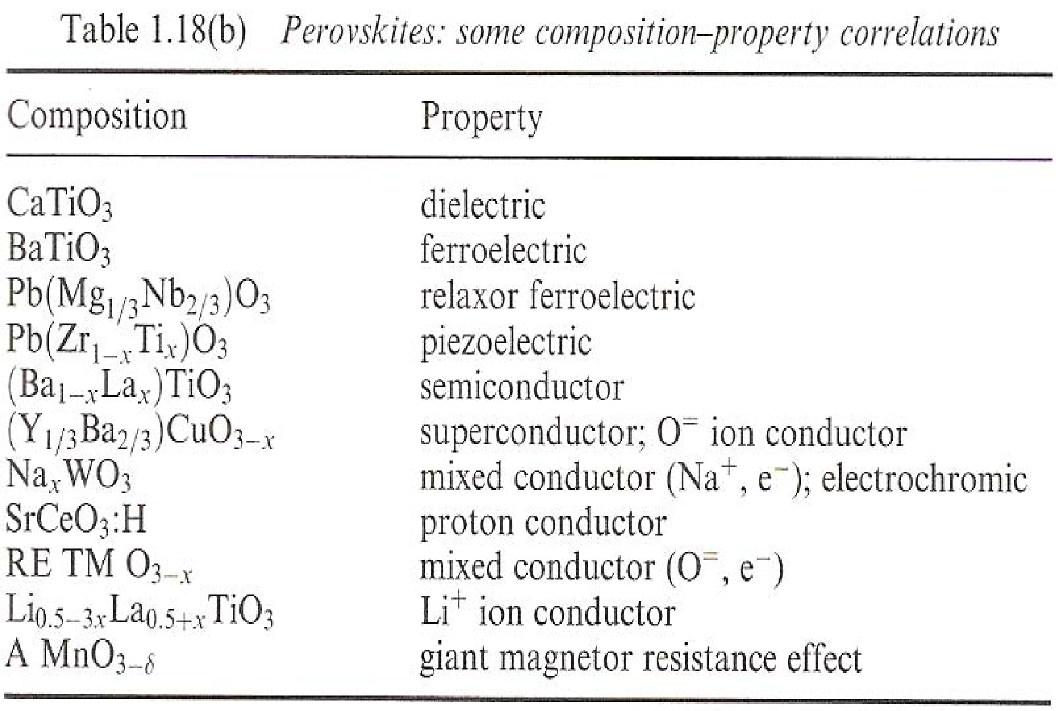


Table 1.18(b) *Perovskites: some composition–property correlations*

Composition	Property
$CaTiO_3$	dielectric
$BaTiO_3$	ferroelectric
$Pb(Mg_{1/3}Nb_{2/3})O_3$	relaxor ferroelectric
$Pb(Zr_{1-x}Ti_x)O_3$	piezoelectric
$(Ba_{1-x}La_x)TiO_3$	semiconductor
$(Y_{1/3}Ba_{2/3})CuO_{3-x}$	superconductor; $O^{=}$ ion conductor
Na_xWO_3	mixed conductor (Na^+, e^-); electrochromic
$SrCeO_3$:H	proton conductor
RE TM O_{3-x}	mixed conductor ($O^{=}$, e^-)
$Li_{0.5-3x}La_{0.5+x}TiO_3$	Li^+ ion conductor
A $MnO_{3-\delta}$	giant magnetor resistance effect

h) Rhenium trioxide (ReO_3) and tungsten bronzes

The cubic ReO_3 structure is the same as the 'TiO_3' framework of perovskite $SrTiO_3$, but without the body center Sr (Re at corners with O at edge centers).

Table 1.19. A few oxides and halides form the ReO_3 structure. Cu_3N has the anti-ReO_3 structure.

Tungsten bronze structures are intermediate between ReO_3 and perovskite. The series Na_xWO_3 have a 3D framework of WO_6 octahedra, as in ReO_3, but with some ($0 < x < 1$) of the large A sites occupied by Na. To accommodate the valence of Na, the formula of the bronzes my be $Na_xW_x^{V}W_{1-x}^{VI}O_3$.

At low x, they are pale green/yellow and semiconducting. As x rises, electrons begin to occupy the 5d band of tungsten, they become metallic, hence the name 'bronze'. A wide variety of monovalent cations enter the structure.

Molybdenum bronzes MoO_3 have similar series.

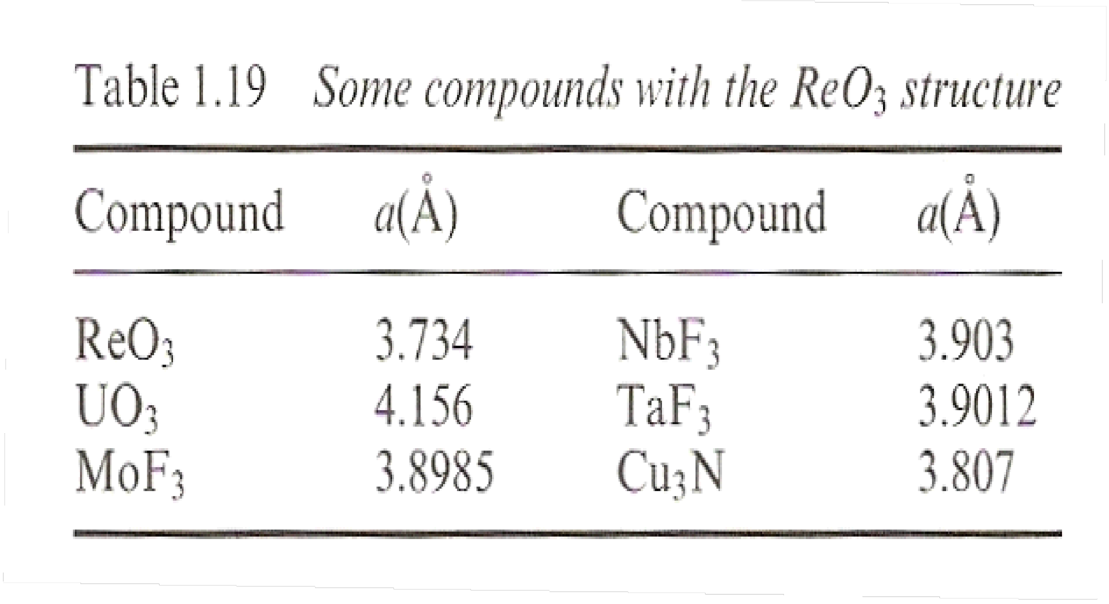


Table 1.19 *Some compounds with the ReO_3 structure*

Compound	a(Å)	Compound	a(Å)
ReO_3	3.734	NbF_3	3.903
UO_3	4.156	TaF_3	3.9012
MoF_3	3.8985	Cu_3N	3.807

i) Spinel (尖晶石)

Several commercially important magnetic oxides have the spinel structure: $MgAl_2O_4$, ccp oxide ions with Mg^{2+}, Al^{3+} in tetrahedral and octahedral interstices, respectively.

Different charge combinations are possible:

2, 3 as in $MgAl_2O_4$; 2, 4 as in Mg_2TiO_4; 1, 3, 4 as in $LiAlTiO_4$; 1, 3 as in $Li_{0.5}Al_{2.5}O_4$; 1, 2, 5 as in $LiNiVO_4$; 1, 6 as in Na_2WO_4.

Sulfides: $ZnAl_2S_4$ and Cu_2SnS_4

Halides: cations are limited to charges of 1 and 2 because cation:anion = 3:4, e.g. Li_2NiF_4.

The unit cell of the spinel structure is a large cube, eight times (2×2×2) the size of fcc. $MgAl_2O_4$ has a large cubic unit cell with a = 8.08Å. The cell contents corresponds to $Mg_8Al_{16}O_{32}$ (Z=8). In the ccp oxide array, 1/2 of the octahedral sites are occupied by Al and 1/8 of the tetrahedral sites (T_+ and T_-) by Mg.

The general formula $A^{tet}B_2^{oct}O_4$. Considering $B_2^{oct}O_4$ first, this is a rock salt structure with ccp O^{2-} but with only alternate octahedral sites occupied by B. Fig. 1.37a,b: subcell (a) on top of subcell (b) in a unit cell. Oxygens are at corners and face centers. Octahedral positions are alternately occupied (solid circle) and empty (square) in any of a, b, c directions. Fig. 1.37c is the base of the unit cell, formed by the base of (b, dasded) and those of three adjacent subcells. The alternating empty-occupied-empty can be observed.

The tetrahedral A cations. According to Fig. 1.20, the tetrahedral sites have equal distance from oxygens and the octahedral cations (9–A and 9–3 are equal). Cation–cation repulsions do not allow adjacent tetral and octahedral sites to be occupied simultaneously. In Fig. 1-37a, all the tetrahedral sites have at least one neighboring octahedral cation, so none of the tetrahedral sites in this subcell is occupied. In Fig. 1.37b, there are two tetrahedral sites for A (no octahedral cation neighbors). Taking the spinel structure as a whole, the octants fall into two groups: (a) and (b), with (b) containing A cations.

The two types of octant are arranged such that they alternate in any of the three unit cell directions (Fig. 1.37d). Fig. 1.37e: a projection of the unit cell onto one face, showing the cations positions. The atom heights are given as multiples of c/8 above the base. Octahedral sites (solid circles) O' cations in (b) are observed. Tetrahedral sites are represented by A.

In practice, the anions are displaced slightly from their corner and face center positions. The bond lengths to A and B cations can change so as to best fit those required by the particular A and B ions. The origin of spinel structure is usually shifted to coincide with a tetrahedral A cation (e.g. the A cations alone are arranged in the same way as the C atoms in the diamond structure).

The cation distribution may vary. Two extreme types of behavior:
Normal spinel: $[A]^{tet}[B_2]^{oct}O_4$ Examples of normal spinels are $MgAl_2O_4$ and $MgTi_2O_4$.
Inverse spinel: $[B]^{tet}[A,B]^{oct}O_4$ half of B ions occupy tetrahedral sites, leaving remaining B ions and all the A ions in octahedral sites. The cations A and B are usually disordered over the octahedral sites. Examples of inverse spinels are $MgFe_2O_4$ and Mg_2TiO_4.
A complete range of intermediate cation distributions is possible and in some cases, the distribution changes with temperature. A parameter, γ, which is the fraction of A ions on the octahedral sites:

Normal:	$[A]^{tet}[B_2]^{oct}O_4$	$\gamma = 0$
Inverse:	$[B]^{tet}[A,B]^{oct}O_4$	$\gamma = 1$
Random:	$[B_{0.67}A_{0.33}]^{tet}[A_{0.67},B_{1.33}]^{oct}O_4$	$\gamma = 0.67$

The degree of inversion, γ, is influenced by the site preference of ions in terms of size, covalent bonding effects and crystal field stabilization energies. The net effect of these parameters leads to the resulting γ. Some compounds with the spinel structure are given in Table 1.20.

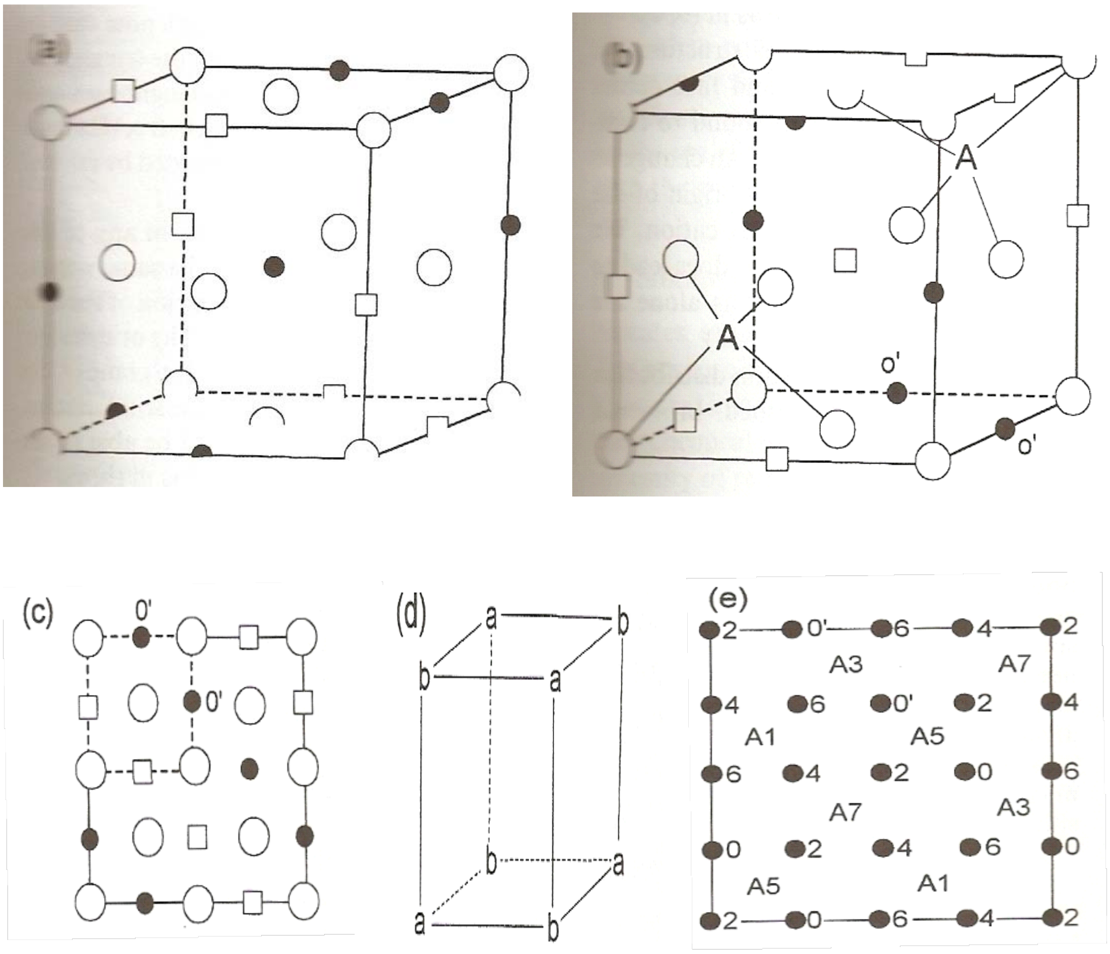


Fig. 1.37 Representative parts of the spinel structure. (a) One octant of the unit cell showing oxygens at corner and face centres, empty □ and occupied (•) octahedral sites. (b) A second octant, underneath the one in (a) showing in addition the occupation of two tetrahedral sites, A. (c) One face of the cubic unit cell of the spinel structure. The dashed part coincides with the base of the subcell shown in (b). (d) Alternating arrangement of the two types of octant (a) and (b). (e) Cation positions in spinel. Numbers refer to fractional heights, as multiples of $c/8$. Oxygens O′ are also shown in (b, c)

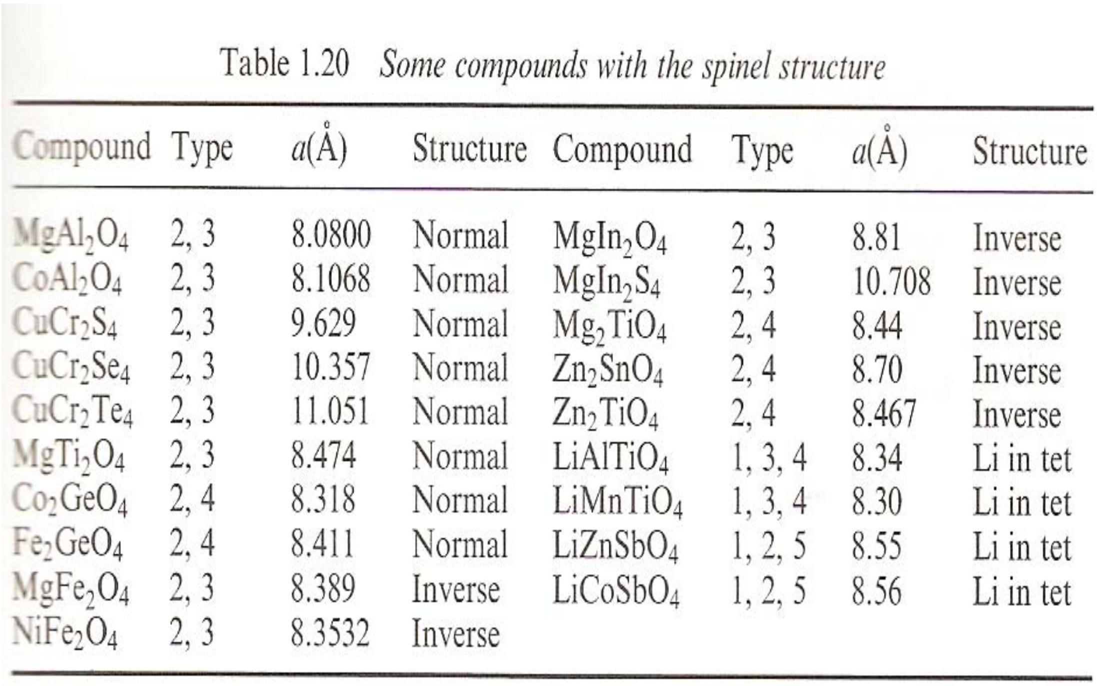


Table 1.20 *Some compounds with the spinel structure*

Compound	Type	a(Å)	Structure	Compound	Type	a(Å)	Structure
$MgAl_2O_4$	2, 3	8.0800	Normal	$MgIn_2O_4$	2, 3	8.81	Inverse
$CoAl_2O_4$	2, 3	8.1068	Normal	$MgIn_2S_4$	2, 3	10.708	Inverse
$CuCr_2S_4$	2, 3	9.629	Normal	Mg_2TiO_4	2, 4	8.44	Inverse
$CuCr_2Se_4$	2, 3	10.357	Normal	Zn_2SnO_4	2, 4	8.70	Inverse
$CuCr_2Te_4$	2, 3	11.051	Normal	Zn_2TiO_4	2, 4	8.467	Inverse
$MgTi_2O_4$	2, 3	8.474	Normal	$LiAlTiO_4$	1, 3, 4	8.34	Li in tet
Co_2GeO_4	2, 4	8.318	Normal	$LiMnTiO_4$	1, 3, 4	8.30	Li in tet
Fe_2GeO_4	2, 4	8.411	Normal	$LiZnSbO_4$	1, 2, 5	8.55	Li in tet
$MgFe_2O_4$	2, 3	8.389	Inverse	$LiCoSbO_4$	1, 2, 5	8.56	Li in tet
$NiFe_2O_4$	2, 3	8.3532	Inverse				

j) Silicate structures– some tips to understanding them

Silicates often have complex formulas and structures. The purpose of this section is to show how structure information may be obtained from their chemical formulas. Some guidelines can appreciate whether a particular silicate is a 3D framework structure, sheetlike, chain-like, etc.

Silicate structure should be regarded as composed of cations and silicate anions. Silicate ions range from isolated SiO_4^{4+} tetrahedral such as in olivine (Mg_2SiO_4) to infinite 3D frameworks as in silica (SiO_2). Certain principles:

(1) Almost all silicates are built of SiO_4 tetrahedra
(2)The tetrahedra link by sharing corners to form larger polymeric units
(3)No more than two SiO_4 tetra may share a common corner (oxygen)
(4)SiO_4 tetrahedra never share edges or faces

Exceptions to (1) are structures in which Si is octahedrally coordinated to O as in one polymorph of SiP_2O_7 and in high pressure polymorphs of SiO_2 (coesite 柯石英, stishovite 超石英).

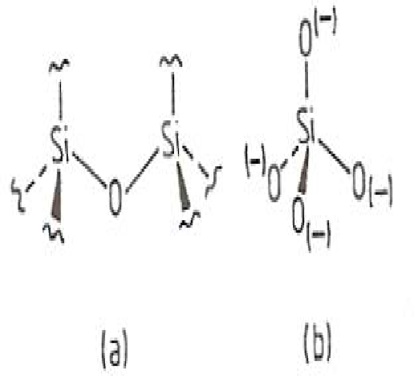
The Si:O ratio relates formula to structure type. Two types of O: bridging oxygens and non-bridging oxygens (Fig. 1.38). The bridging oxygens belong half to one Si and the non-bridging oxygens are terminal oxygens, must being linked to other cations in the crystal structure. In evaluating the net Si:O ratio, bridging oxygens count as 1/2 and non-bridging oxygen as 1. The overall Si:O in silicates depends on the relative numbers of bridging and non-bridging oxygens (Table 1.21).

Many more complex examples can be given in addition to those in Table 1.21. Ex.: $Na_2Si_3O_7$, the Si:O = 1: 2.33, this corresponds to in a SiO_4 tetrahedron, 3 O is bridging and 2/3 and 1/3 of an O is non-bridging and bridging, respectively. The structure of the silicate ion is expected to be something between a sheet and a 3D framework. In fact, it is an infinite, double-sheet silicate anion in which 2/3 of the SiO_4 tetrahedra have one non-bridging O.

The structure is more complex when Al is present. Two categories: Al substitutes for Si in the tetrahedral; Al occupies octahedral sites. $NaAlSi_3O_8$ (albite 鈉長石) and $CaAl_2Si_2O_8$ (anorthite 鈣長石), Al partly replaces Si. It is appropriate to consider (Si+Al):O, which is 1:2. So, a 3D framework is expected.

Substitution of Al for Si occurs in many sheet structures such as micas and clay minerals. Talc ($Mg_3(OH)_2Si_4O_{10}$, 滑石,雲母) has an Si:O ratio of 1:2.5, and the structure contains infinite silicate sheets. In mica phlogopite 金雲母, 1/4 of Si in talc is replaced by Al and extra K is added to preserve electroneutrality, i.e. $KMg_3(OH)_2(Si_3Al)O_{10}$. In talc and phlogopite, Mg occupies octahedral sites between silicate sheets; K occupies 12-coordinate sites. In mica muscovite 白雲母 ($KAl_2(OH)_2(Si_3Al)O_{10}$), it contains infinite sheets $(Si_3Al)O_{10}$. However, two other Al^{3+} replace the three Mg^{2+} of phlogopite and occupy the octahedral sites. Only ions replacing Si in tetrahedra are included as part of the complex anion. Hence octahedral Al^{3+} are regarded as cations.

With a few exceptions, silicate structure cannot be described as cp. The clear identification of the silicate anion component facilitates classification and description of a very range of structures. In addition, the Si–O bond is strong and partially covalent. The consequent stability of silicate anion is responsible for many properties.



(a) (b)

Fig. 1.38 Silicate anions with (a) bridging and (b) non-bridging oxygens

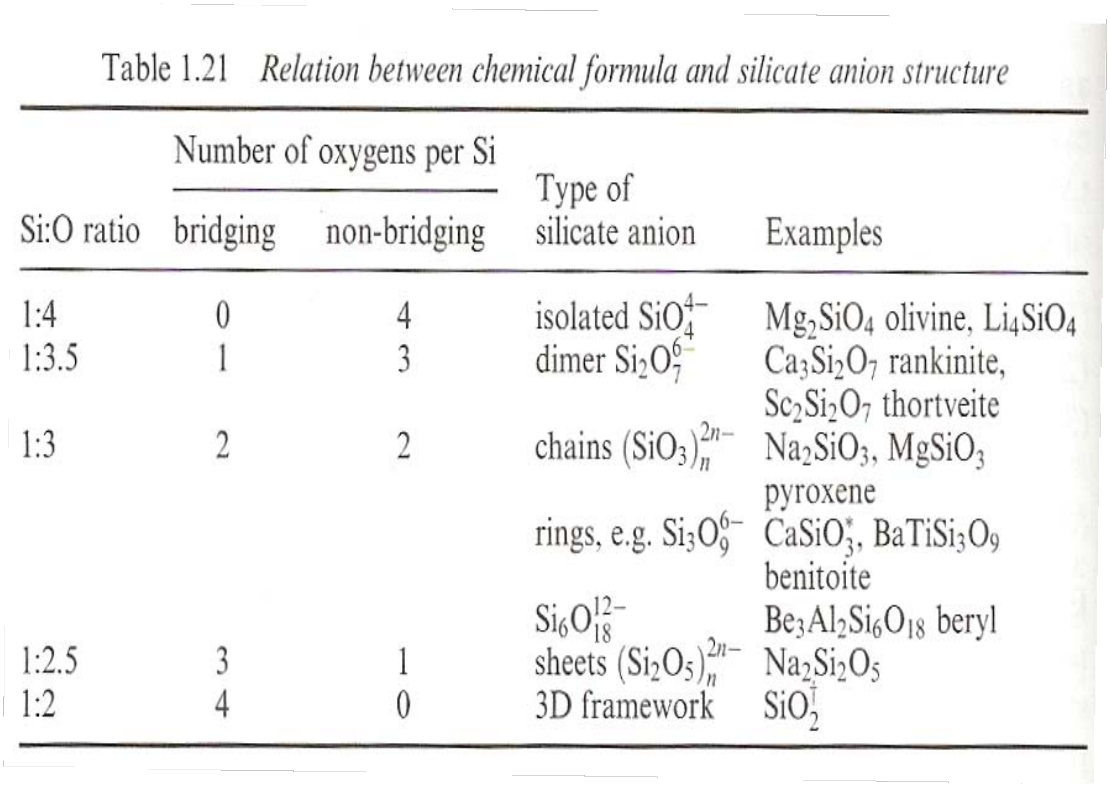


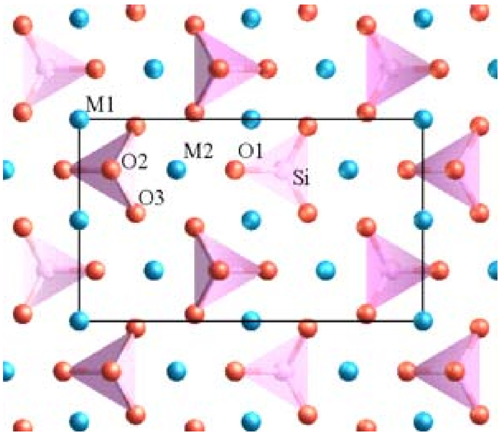
Table 1.21 *Relation between chemical formula and silicate anion structure*

	Number of oxygens per Si			
Si:O ratio	bridging	non-bridging	Type of silicate anion	Examples
1:4	0	4	isolated SiO_4^{4-}	Mg_2SiO_4 olivine, Li_4SiO_4
1:3.5	1	3	dimer $Si_2O_7^{6-}$	$Ca_3Si_2O_7$ rankinite, $Sc_2Si_2O_7$ thortveite
1:3	2	2	chains $(SiO_3)_n^{2n-}$	Na_2SiO_3, $MgSiO_3$ pyroxene
			rings, e.g. $Si_3O_9^{6-}$	$CaSiO_3^*$, $BaTiSi_3O_9$ benitoite
			$Si_6O_{18}^{12-}$	$Be_3Al_2Si_6O_{18}$ beryl
1:2.5	3	1	sheets $(Si_2O_5)_n^{2n-}$	$Na_2Si_2O_5$
1:2	4	0	3D framework	$SiO_2^\dagger$

Minerals in the olivine group crystallize in the orthorhombic system (space group P*bnm*) with isolated silicate tetrahedra, meaning that olivine is a nesosilicate. In an alternative view, **the atomic structure can be described as a hexagonal, close-packed array of oxygen ions with half of the octahedral sites occupied with magnesium or iron ions and one-eighth of the tetrahedral sites occupied by silicon ions.**

There are three distinct oxygen sites (marked O1, O2, and O3 in figure 1), two distinct metal sites (M1 and M2), and only one distinct silicon site. O1, O2, M2, and Si all lie on mirror planes, while M1 exists on an inversion center. O3 lies in a general position.

Olivine Mg_2SiO_4



This figure shows the atomic scale structure of olivine looking along the *a* axis (P*bnm* setting) with the long *b* axis across the page and the short *c* axis up the page. Oxygen is shown in red, silicon in pink and magnesium/iron in blue, the three inequivelent oxygen, and two inequivelent metal sites are marked O and M respectivly. A projection of the unit cell is shown by the black rectangle