(ii) Relative sizes of tetrahedral and octahedral sites

—A general guideline for the relative size of sites:

tetrahedra $<$ octahedra $<$ polyhedra of higher coordination number

—In ionic structures, cations M occupy those sites of suitable sizes.

—Cations may occupy sites which appear too small by pushing apart anions and expanding the structure (as in eutectic structures).

—Cations tend not to occupy sites that are too large, unless the structure can adjust itself, by twisting or distorting the anion array so as to reduce the size of the sites.

—In many distorted perovskite structures in which cations are too small to occupy large 12-coordinate site and a partial structure collapse occurs.

—In some cases, a cation site is marginally too large, the cation can then undergo small displacements giving rise to high polarizability, high permittivity and the phenomenon of ferroelectricity.

(iii) Location of tetrahedral and octahedral sites in an *fcc* unit cell; bond length calculations; fractional atomic coordinates

Fig. 1.20 An *fcc* anion array (cation sites 1–12)

—The T_+, T_- and O sites are located within an *fcc* unit cell that has anions, X, at corners and face centers.

—The octahedral sites are easiest to locate: at edge-center 1, 2, 3 and body-center 4 positions.

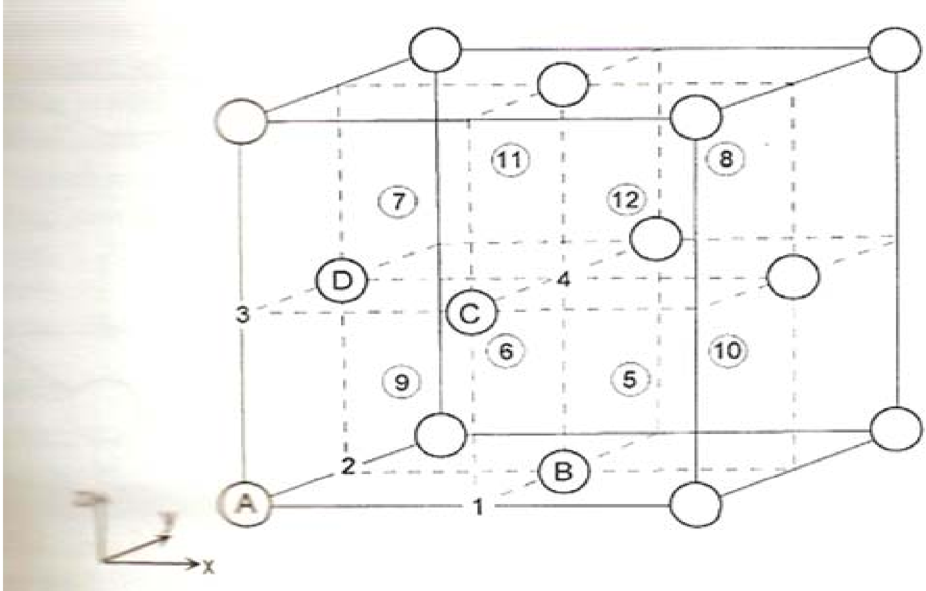


Fig. 1.20 Available cation sites, 1–12, in an *fcc* anion array

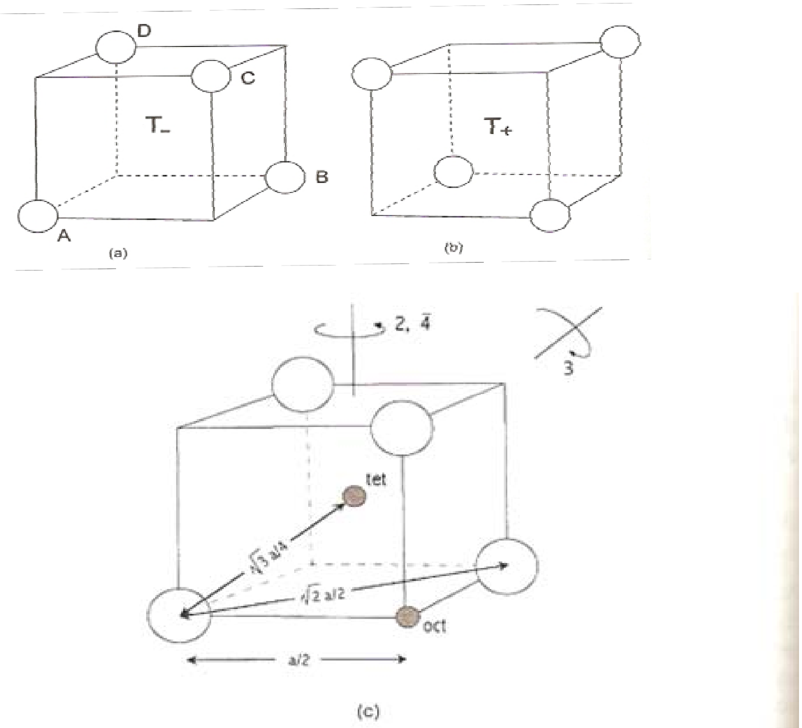


Fig. 1.21 (a, b) Tetrahedral sites T_+, T_- and their relation to a cube. (c) Bond length calculations and some symmetries of a tetrahedron

—In order to see the T_+, T_- sites, we divide the unit cell into eight minicubes, which contain anions at only four of the eight corners. In the middle of each minicube is a tetrahedral site.

—There are two orientations for the minicubes, as shown in Fig.1.21.

—In Fig.1.21a, the T_- tetrahedra have their apices pointing in the $[\bar{1}\,\bar{1}\,\bar{1}]$ and in Fig.1.21b the T_+ sites in the [111] direction.

—It is exceptionally useful to regard a tetrahedral site as occupying the center of a cube with alternate corners absent, Fig.1.21a,b.

—Fig.1.21c, the minicube

*edge dimension = a/2

*M–X = bond length = $\frac{1}{2}\sqrt{(\sqrt{2}\frac{a}{2})^2+(\frac{a}{2})^2}=\frac{1}{2}\sqrt{3(\frac{a}{2})^2}=\frac{\sqrt{3}}{4}a$

*2-fold rotation axes and $\bar{4}$ (fourfold inversion) axes run parallel to minicube edges but pass through pairs of opposite faces; three of these in total.

*mirror planes occur parallel to the set of lattice planes with indices {110}; six of these in total.

*3-fold axes run parallel to <111> directions; four in total.

—The fractional coordinates of the atoms in Fig.1.20

*an *fcc* unit cell has effectively 4 anions in the cell:

One at the corner and three at face centers, A, B, C, D

i.e. 000 $\frac{1}{2}\frac{1}{2}0$ $\frac{1}{2}0\frac{1}{2}$ $0\frac{1}{2}\frac{1}{2}$

—000 : eight equivalents, $\frac{1}{8}$ of each belongs to the cell

$\frac{1}{2}\frac{1}{2}0,\ \frac{1}{2}0\frac{1}{2},\ 0\frac{1}{2}\frac{1}{2}$ **:** six equivalents, $\frac{1}{2}$ of each belongs to the cell

—Cation positions

Octahedral $1:\frac{1}{2}00 \quad 2:0\frac{1}{2}0 \quad 3:00\frac{1}{2} \quad 4:\frac{1}{2}\frac{1}{2}\frac{1}{2}$

Tetrahedral, T_+ $5:\frac{3}{4}\frac{1}{4}\frac{1}{4} \quad 6:\frac{1}{4}\frac{3}{4}\frac{1}{4} \quad 7:\frac{1}{4}\frac{1}{4}\frac{3}{4} \quad 8:\frac{3}{4}\frac{3}{4}\frac{3}{4}$

Tetrahedral, T_- $9:\frac{1}{4}\frac{1}{4}\frac{1}{4} \quad 10:\frac{3}{4}\frac{3}{4}\frac{1}{4} \quad 11:\frac{1}{4}\frac{3}{4}\frac{3}{4} \quad 12:\frac{3}{4}\frac{1}{4}\frac{3}{4}$

—four of each type of cation site, O, T_+, T_- in the unit cell together with four anions

—When different sites are fully or partially occupied by cations, different structures are generated.

(d) Covalent network structures

Materials such as diamond and silicon carbide, which have very strong, directional, covalent bonds, can also be described as *cp* structures or eutectic structures.

e.g. a polymorph of SiC having the wurtzite structure

it is immaterial whether Si or C is regarded as the packing atom; since the net result, a 3D framework of corner-sharing tetrahedra, is the same.

e.g. diamond

- can be regarded as a sphalerite structure in which half the C atoms form a *ccp* array and the other half occupy T_+ sites.
- the two types of atom are equivalent
- diamond should be classified as a eutectic structure; it is unrealistic distinguish between packing atoms and interstitial atoms

Many structures have mixed ionic-covalent bonding, e.g. ZnS and $CrCl_3$, and they can be described in terms of *cp* without reference to the type of bonding that is present.

(e) Molecular structures

Many molecular compounds crystallize as *cp* structures even though the forces between adjacent molecules are weak van der Waals forces.

If the molecules are roughly spherical or become spherical because they can rotate or occupy different orientations at random, then simple *hcp* or *ccp* structures result (e.g. crystalline H_2, CH_4 and HCl).

Non-spherical molecules, especially if they are built of tetrahedra or octahedra, can also fit into a *cp* arrangement.

Ex. Al_2Br_6: a dimer with two $AlBr_4$ tetrahedra sharing a common edge (Fig 1.22a). Br atoms 3 and 5 are common to both tetrahedra and are the bridging atoms.

In crystalline Al_2Br_6, the Br atoms form an *hcp* array and Al atoms occupy 1/6 of the tetrahedral sites (Fig 1.22b).

each Br has T_+ T_- (2) sites
Al occupied 1/6 T-sites
→$(\frac{1}{6} * 2)$ Br atoms
→Al : Br = $\frac{1}{3}$: 1

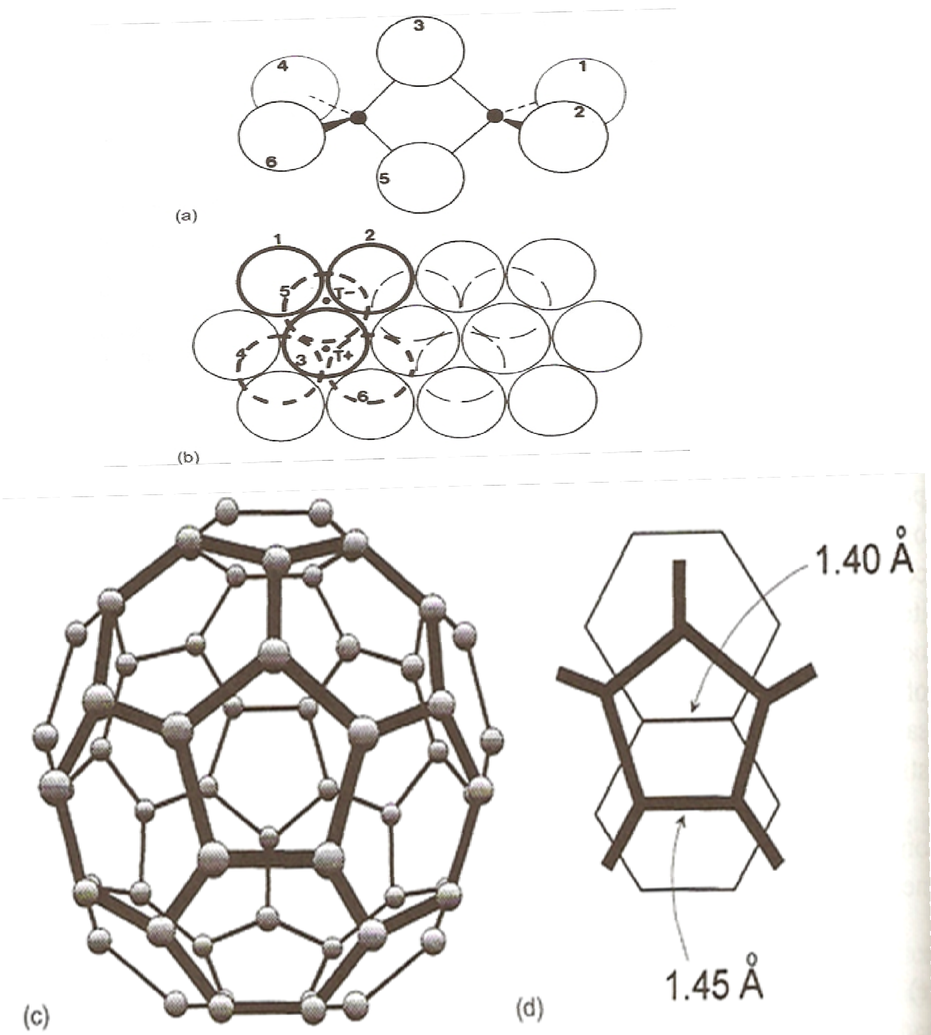


Fig. 1.22 (a) *hcp* arrangement of Br atoms in crystalline Al_2Br_6; (b) Al atoms occupy T_+ and T_- sites. Dashed circles are below the plane of the paper. (c) The C_{60} molecule; one pentagon surrounded by five hexagons is shown in bold. (d) Parts of two C_{60} molecules in the region of closest contact showing a short C–C bond separating two hexagons in one molecule pointing towards the middle of a pentagon in an adjacent molecule. (Adapted from David *et al.*, *Nature*, **353**, 147, 1991)

Fig 1.22b shows one molecule Al_2Br_6 (Br in heavy outline) in a *cp* array. Al atoms occupy one pair of adjacent T_+ and T_- sites.

Adjacent Al_2Br_6 molecules are arranged so that each Br in the *hcp* array belongs to only one molecule.

$SnBr_4$: a tetrahedral molecule and crystallize with an *hcp* Br array. 1/8 of the tetrahedral sites are occupied.

(f) Fullerenes and fullerides

Simplest, most well-known and symmetrical fullerene is C_{60}

Fig 1.22c —a hollow, spherical cage of diameter 7.1Å

—formed from 3-coordinate C atoms (approximately sp^2 hybridized)

—a network of 12 pentagons and 20 hexagons

—match the pattern on a soccer ball, American name "buckyball"

("fullerene" is in honor of Buckminster Fuller who designed the geodesic dome that has the same network structure as C_{60})

Crystalline C_{60}: C_{60} molecules are arranged in close packing at room temperature

—face centered cubic, Z = 4(C_{60}), a = 14.17Å

C_{60} molecules are orientationally disordered at room temp.

—Fig.1.18(a) $2r = \sqrt{2}\,a = 20Å$

→r = distance between centers of adjacent C_{60} = 10Å

→gap = 10Å – 7.1Å = 2.9Å

At T < 249K, ordered arrangement of C_{60} molecules

—driving force for this ordering

the short electron-rich C-C bond that links two hexagons in one C_{60} points directly at the center of an electron-deficient pentagon (Fig.1.22(d))

—this arrangement minimizes direct C-C overlap but maximizes donor-acceptor interactions

—two groups of bonds in C_{60}:

1.40Å for C-C bonds linking two hexagons

1.45Å for C-C bonds linking one hexagon and one pentagon

ps. Single and double bond length of C-C in organics are 1.54 and 1.33Å, respectively.

Other fullerenes, such as C_{70}

—also form *cp*, even though they are not spherical

—C_{70} is an ellipsoid (rugby ball, long axis = 8.34Å, short axis = 7.66Å)

—at room temperature, the ellipsoids rotate freely to give quasi-spherical molecules and form an *fcc* structure, a = 15.01Å

Fullerides: tetrahedral and octahedral interstitial sites of C_{60} occupied by large alkali cations (like Rb, rubidium)

A_3C_{60} (as in Rb_3C_{60} or K_2RbC_{60})
—all T_+, T_- and O sites are occupied
—they are metallic since alkali metals ionize and donate e^- to the conduction band of the C_{60} network, which is half-full in A_3C_{60}.
—at low temperatures, many fullerides become superconducting.

AC_{60} (rock salt or zinc blende analogues)

A_2C_{60} (fluorite analogues)

A_4C_{60} (A = Na, A_4 clusters form in the octahedral sites)

A_6C_{60} (the packing of C_{60} changes from *ccp* to *bcc*)
—*bbc* has a large number of interstitial sites
—6 distorted tetrahedral sites distributed over the cube faces

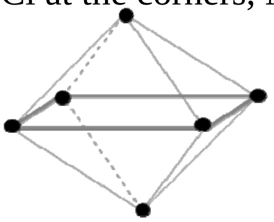
The excitement in C_{60} chemistry
—C_{60} can accept a number of e^- to give anions C_{60}^{n-}
—electronic properties range from insulating to metallic/superconducting, depending on the value of n.

1.16 Structures built of space-filling polyhedra

This approach emphasizes the coordination number of cations; structures are built of polyhedra (cation + anionic neighbors); polyhedra link by sharing corners, edges, or faces.

Example: NaCl (Na has six Cl nearest neighbors arranged octahedrally)

an octahedron: Cl at the corners, Na at the center



A 3D overview of NaCl, each octahedron edge is shared between two octahedra (Fig.1.26, see later), resulting in an infinite framework.

Example: Perovskite $SrTiO_3$

TiO_6 octahedra link by corner-sharing to form a 3D framework (Fig.1.36, see later)

Very many other crystals involve mainly tetrahedra and octahedra, leading to a wide diversity of structures (Table 1.5)

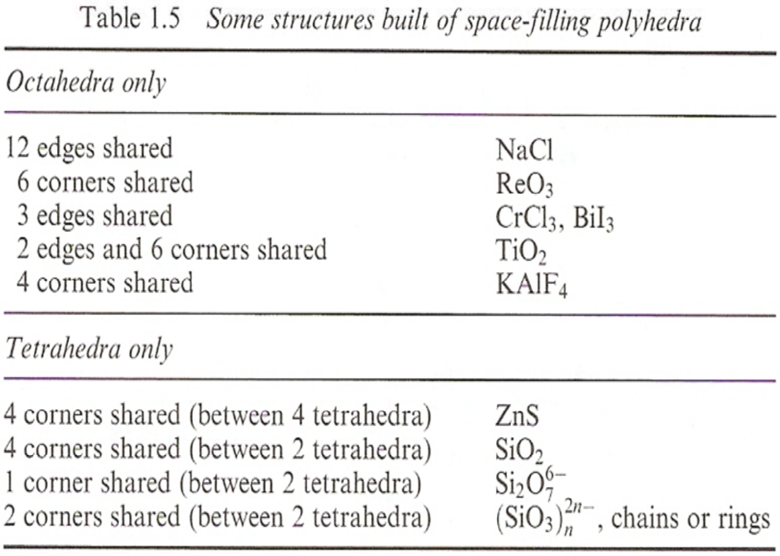


Table 1.5 *Some structures built of space-filling polyhedra*

Octahedra only	
12 edges shared	NaCl
6 corners shared	ReO_3
3 edges shared	$CrCl_3$, BiI_3
2 edges and 6 corners shared	TiO_2
4 corners shared	$KAlF_4$
Tetrahedra only	
4 corners shared (between 4 tetrahedra)	ZnS
4 corners shared (between 2 tetrahedra)	SiO_2
1 corner shared (between 2 tetrahedra)	$Si_2O_7^{6-}$
2 corners shared (between 2 tetrahedra)	$(SiO_3)_n^{2n-}$, chains or rings

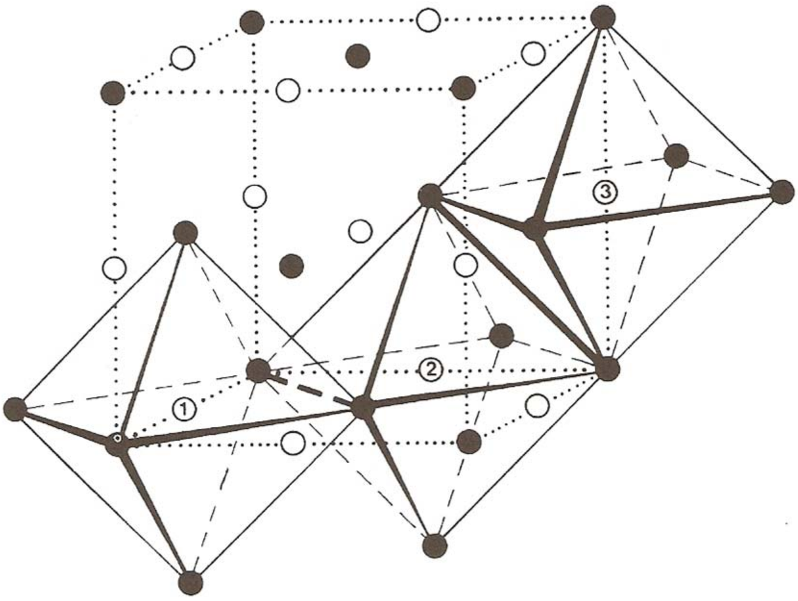


Fig. 1.26 Unit cell of the rock salt structure showing edge-sharing octahedra

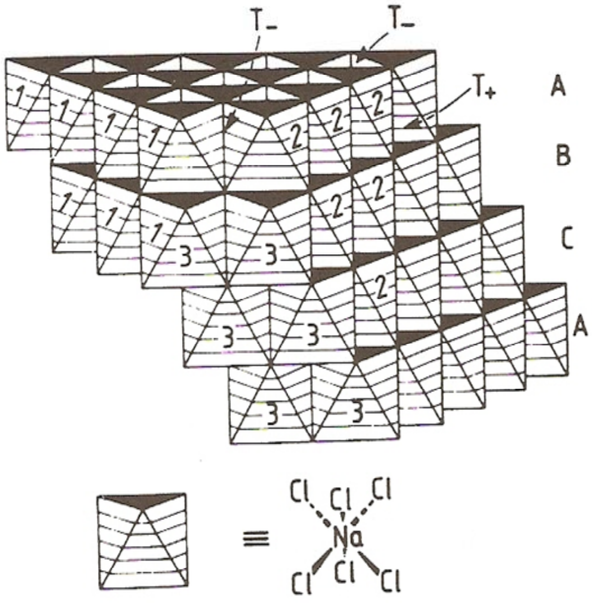


Fig. 1.27 The rock salt structure as an array of edge-sharing octahedra

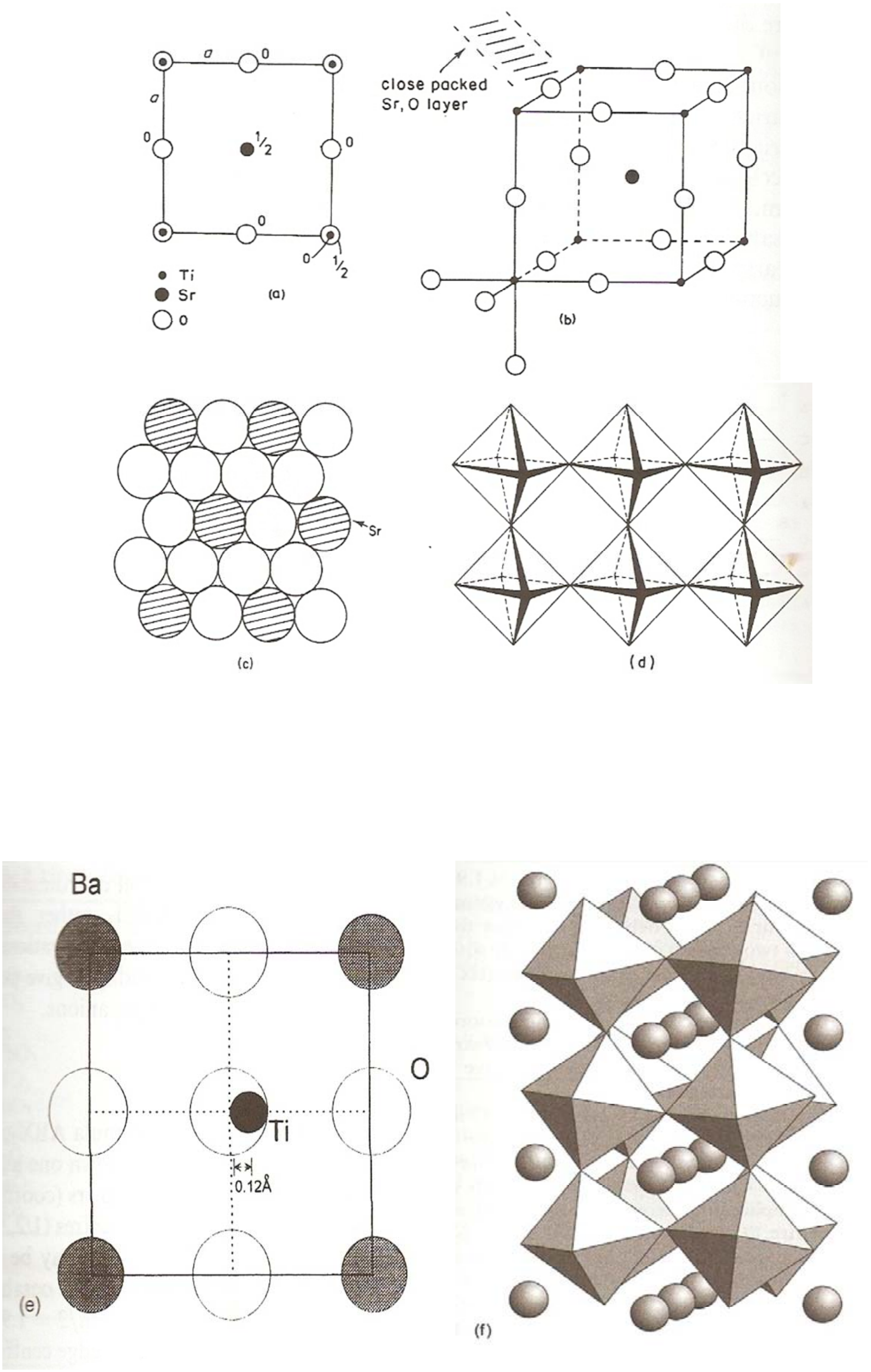


Fig. 1.36 (a–d) The perovskite structure of $SrTiO_3$. (e) Structure of tetragonal $BaTiO_3$ projected onto the *ac* plane. (From Weller, *Inorganic Materials Chemistry*, 1994.) Note, the origin of the unit cell is shifted to coincide with Ba rather than with Ti as in (a). (f) $GdFeO_3$ structure

We cannot estimate the efficiency of packing spheres for space-filling polyhedra since the anions (usually the largest) are represented by points. However, the space-filling polyhedron approach shows the topology or connectivity of a framework and indicates clearly the location of interstitial sites.

The Variables for Space-Filling Polyhedron Approach

Polyhedra: tetrahedra, octahedra, trigonal prisms, …

Link: share some or all of their corners, edges and faces with adjacent polyhedra. Corners and edges may be common to two or more polyhedra, but only two can share a common face.

Some important points:

1) The bonding forces between atoms or ions are not taken into account for topological approach to arrange polyhedra.
2) The polyhedron entities do not necessarily exist.

   e.g. $NaCl_6$ in NaCl ionic network and SiC_4 in covalent SiC network not exist

   e.g. molecular Al_2Br_6 (containing pairs of edge-sharing tetrahedra) exist; complex ions SiO_4 tetrahedra range from monomers to infinite chains.

Principles for Polyhedral linkages

Shared edges and faces decrease the stability of a structure, particularly for cations of high valence and small coordination number.

1) Decrease in the cation-cation distance (i.e. distances between the centers of polyhedra) due to sharing can lead to the cations repelling each other electrostatically.

2) Fig. 1.23 (a and b). The cation-cation distance is less in edge sharing than in corner sharing.
3) Fig. 1.23 (b and c). The cation-cation distance M–M is less between tetrahedra than between octahedra because the MXM bridge angle is 71º for the former (M–M = 1.16 M–X) and 90º for the latter (M–M = 1.414 M–X).
4) Table 1.6 shows the maximum possible M–M distances for various polyhedral linkages (as a function of M–X). The M–M distance is greatest for corner-sharing and least for face-sharing octahedra.
5) Reduced distance occurs if the polyhedra are rotated about the shared corner or edge (e.g. the MXM angle between corner-shared polyhedra is less than 180º).
6) Table 1.6, face-shared tetrahedra: M–M is less than M–X, this unstable situation does not normally occur.
7) Tetrahedra containing cations of high charge, edge sharing is energetically unstable and only corner sharing occurs. e.g. in silica built of SiO_4 tetrahedra, edge sharing never occurs.

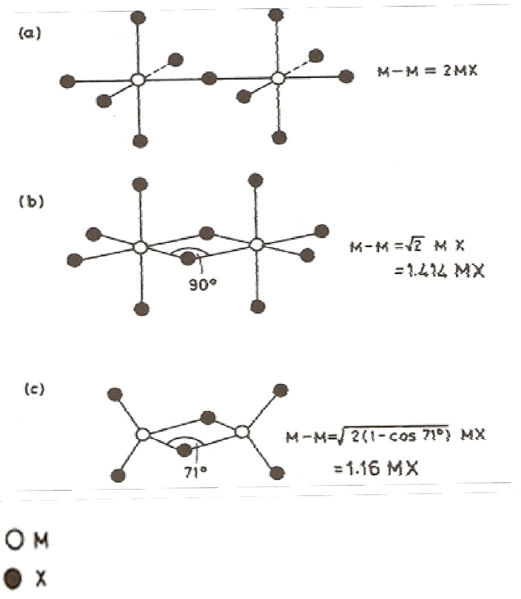


Fig. 1.23 Cation–cation separation in octahedra which share (a) corners and (b) edges and in (c) tetrahedra which share edges

Table 1.6 *The distance M–M between MX_4 or MX_6 groups sharing X atom(s)*

	Corner sharing	Edge sharing	Face sharing
Two tetrahedra	2.00 MX(tet.)*	1.16 MX(tet.)*	0.67 MX(tet.)
Two octahedra	2.00 MX(oct.)*	1.41 MX(oct.)*	1.16 MX(oct.)

* Maximum possible value.