

CHEMISTRY OF INORGANIC OXIDES

19.1 INTRODUCTION

Some oxides can react directly with water to form an acidic, basic, or amphoteric solution. An **amphoteric** solution is a substance that can chemically react as either acid or base. However, it is also possible for an oxide to be neither acidic nor basic. There are different properties which help distinguish between the three types of oxides. The term **anhydride** ("without water") refers to compounds that assimilate H_2O to form either an acid or a base upon the addition of water.

Oxides are binary compounds of oxygen with another element, e.g., CO_2 , SO_2 , CaO , CO , ZnO , BaO_2 , H_2O , etc. these are termed as oxides because here, oxygen is in combination with only one element. Based on their acid-base characteristics oxides are classified as acidic or basic. An oxide that combines with water to give an acid is termed as an acidic oxide. The oxide that gives a base in water is known as a basic oxide.

(i) Acidic oxides

Acidic oxides are the oxides of non-metals (groups 14-17). These acid anhydrides or acidic oxides form acids with water:

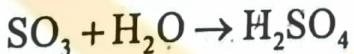
- Sulfurous Acid



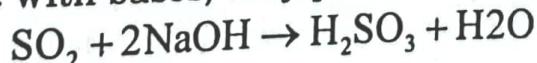
- Carbonic Acid



- Sulfuric Acid

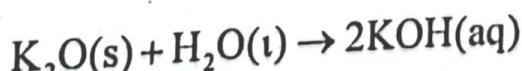


Acidic oxides are, therefore, known as acid anhydrides, e.g., sulfur dioxide is sulfurous anhydride; sulfur trioxide is sulfuric anhydride. When these oxides combine with bases, they produce salts, e.g.,

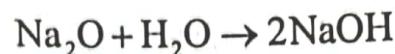
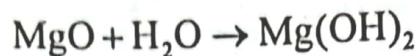
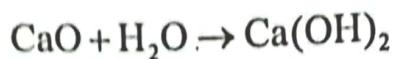


(ii) Basic oxides

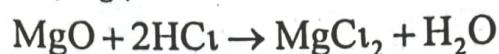
Generally Group 1 and Group 2 elements form bases called bases anhydrides or basic oxides e.g.,



Basic oxides are the oxides of metals. If soluble in water they react with water to produce hydroxides (alkalies) e.g.

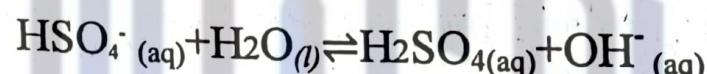
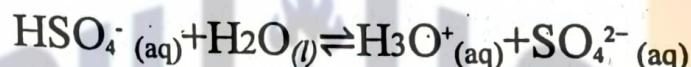


These metallic oxides are therefore, known as basic anhydrides. They react with acids to produce salts, e.g.,

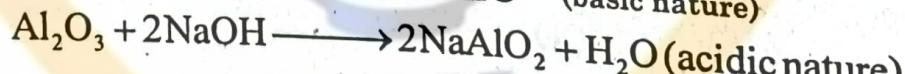
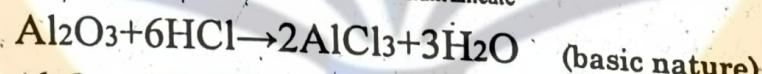
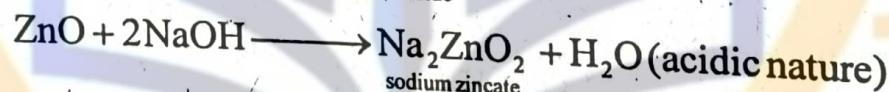


(iii) Amphoteric oxides

An amphoteric solution is a substance that can chemically react as either acid or base. For example, when HSO_4^- reacts with water it can make hydronium ions.



Amphoteric oxides are metallic oxides, which show both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties, e.g.,



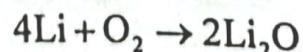
Amphoteric oxides have both acidic and basic properties. A common example of an amphoteric oxide is aluminum oxide. In general, amphoteric oxides form with metalloids.

(iv) Neutral oxides

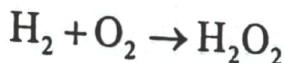
These are the oxides, which show neither basic nor acidic properties, that is, they do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

(v) Peroxides and dioxides

(a) Oxides: Group 1 metals react rapidly with oxygen to produce several different ionic oxides, usually in the form of M_2O , with the oxygen exhibiting an oxidation number of -2.



(b) **Peroxides:** Often lithium and Sodium reacts with excess oxygen to produce the peroxide, M_2O_2 . With the oxidation number of the oxygen equal to -1.



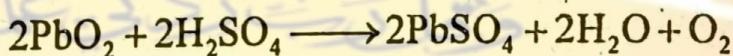
(c) **Super oxides:** Often Potassium, Rubidium, and Cesium react with excess oxygen to produce the superoxide, MO_2 . With the oxidation number of the oxygen equal to -1.



A peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.

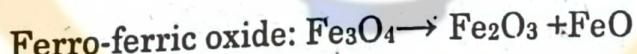
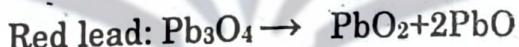


Dioxides like PbO_2 and MnO_2 also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl_2 and on reacting with concentrated H_2SO_4 yield O_2 .

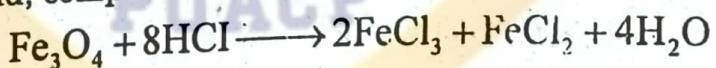


(vi) Compound oxides.

Compound oxides are metallic oxides that behave as if they are made up of two oxides, one that has lower oxidation and one with a higher oxidation of the same metal, e.g.,



On treatment with an acid, compound oxides give a mixture of salts.

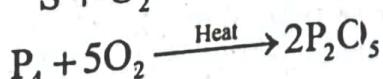
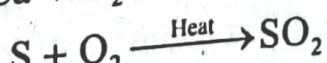
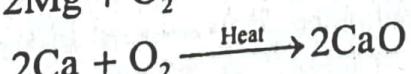
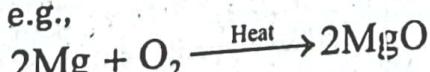


19.2 PREPARATION OF OXIDES

Oxides can be generated via multiple reactions. Below are few.

(i) By direct heating of an element with oxygen

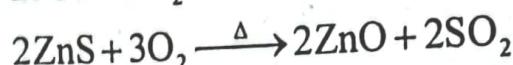
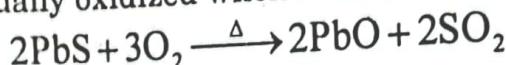
Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,



(ii) By reaction of oxygen with compounds at higher temperatures

At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

- Sulfides are usually oxidized when heated with oxygen.



- When heated with oxygen, compounds containing carbon and hydrogen are oxidized.



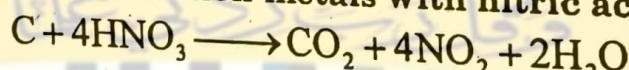
- By thermal decomposition of certain compounds like hydroxides, carbonates, and nitrates



(iii) By oxidation of some metals with nitric acid

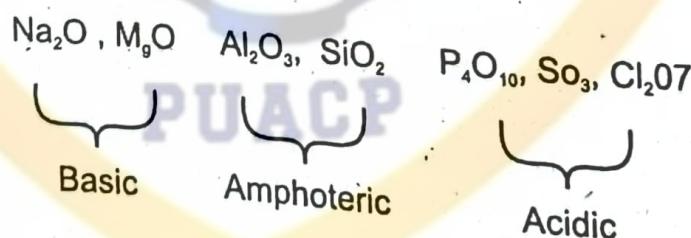


(iv) By oxidation of some non-metals with nitric acid

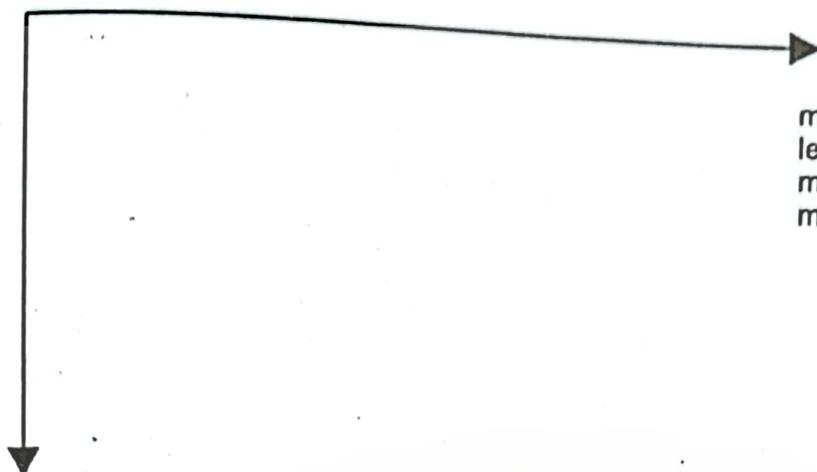


19.3 PERIODIC TRENDS IN ACID-BASE BEHAVIOR

The oxides of elements in a period become progressively more acidic as one goes from left to right in a period of the periodic table. For example, in third period, the behavior of oxides changes as follows:



If we take a closer look at a specific period, we may better understand the acid-base properties of oxides. It may also help to examine the physical properties of oxides, but it is not necessary. Metal oxides on the left side of the periodic table produce basic solutions in water (e.g. Na_2O and MgO). Non-metal oxides on the right side of the periodic table produce acidic solutions (e.g. Cl_2O , SO_3 , P_4O_{10}). There is a trend within acid-base behavior; basic oxides are present on the left side of the period. Acidic oxides are found on the right side. However, this trend yield the question of where and when does the shift occur? The figure below shows how, as we move from left to right, the oxides are more acidic and as we move from top to bottom, the oxides are more basic.



Aluminum oxide shows acid and basic properties of an oxide, it is amphoteric. Thus Al_2O_3 entails the making point at which a change over from a basic oxide to acidic oxide occurs. It is important to remember that the trend only applied for oxides in their highest oxidation states. The individual element must be in its highest possible oxidation state because the trend does not follow if all oxidation states are included. Notice how the amphoteric oxides of each element (grey shade in following table) signify the change from basic to acidic oxides.

Groups: 1 2 3 14 15 16 17

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Bi	Po	At

The table above shows oxides of the s-and p-block elements.

There are three nonmetal oxides from the upper right portion of the periodic table, CO , NO , and N_2O , which have such low oxidation numbers for the central atom that they give neutral aqueous solutions. Since the acidity of a cation rises rapidly with charge, d-block elements which exhibit a wide variety of oxidation numbers may have one or more oxides that exhibit only basic properties and one or more oxides that exhibit only acidic properties. The higher the oxidation number the more acidic the corresponding oxide. Chromium is an example of such an element.

Oxide	Oxidation Number	Category
CrO	Cr^{2+}	basic
Cr_2O_3	Cr^{3+}	amphoteric
CrO_3	Cr^{6+}	acidic

The table below compares the predicted coordination numbers for the atoms with those observed along with the observed lattice types and melting points of the oxides for the elements of Period 3 and the early elements of Period 6.

The following trends can be seen in the properties of oxides in periodic table:

- (i) The valencies of the elements with oxygen rise from 1 to 7.
- (ii) The oxides become more volatile across the period.
- (iii) Those on the left are solids at room temperature; those on the right are gases or liquids.
- (iv) The structure of the oxides changes from ionic to simple molecular.
- (v) The nature of the oxides changes from basic to acidic.
- (vi) The oxides of the metals on the left are basic.
- (vii) The oxides of the non-metals on the right are acidic.
- (viii) Aluminum oxide is both basic and acidic.
- (ix) Oxides which are both basic and acidic are called amphoteric oxides.

Predictions of Physical Properties and Structures of Some Oxides

Period 3	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇	
Radius ratio	0.921	0.683	0.532	0.429	0.413	0.341	0.325	
Predicted C.N of metal	4	6	6	6 or 4	4	4	4	
C.N of oxide	8	6	4	3 or 2	1.6	1.33	1.14	
Observed C.N of metal	4	6	6	4	4	4	4	
C.N of oxide	8	6	4	2	1.6	1.33	1.14	
Lattice type	antiflourite	NaCl	corundum	beta-silica	oligomer	oligomer	molecular	
Melting point	(1275)	2800	2050	1723	(300)	17	91	
Period 6	Cs ₂ O	BaO	Lu ₂ O ₃	HfO ₂	Ta ₂ O ₅	WO ₃	Re ₂ O ₇	OsO ₄
Radius ratio (Inverse " ")	1.437 (0.696)	1.183 (0.846)	0.793	0.675	0.619	0.587	0.537	0.476
Predicted C.N of metal	3	8	8	6	6	6	6	6
C.N of oxide	6	8	5.33	3	2.4	2	1.71	1.5
Observed C.N of metal	3	6	7	8	6	6	5	4
C.N of oxide	6	6	4.67	4	2.4	2	1.42	1
Lattice type	•	NaCl	•	Rutile	•	•	2-dim polymer	molecular
Melting point	490	1920	2487	2900	1870	1473	296	40

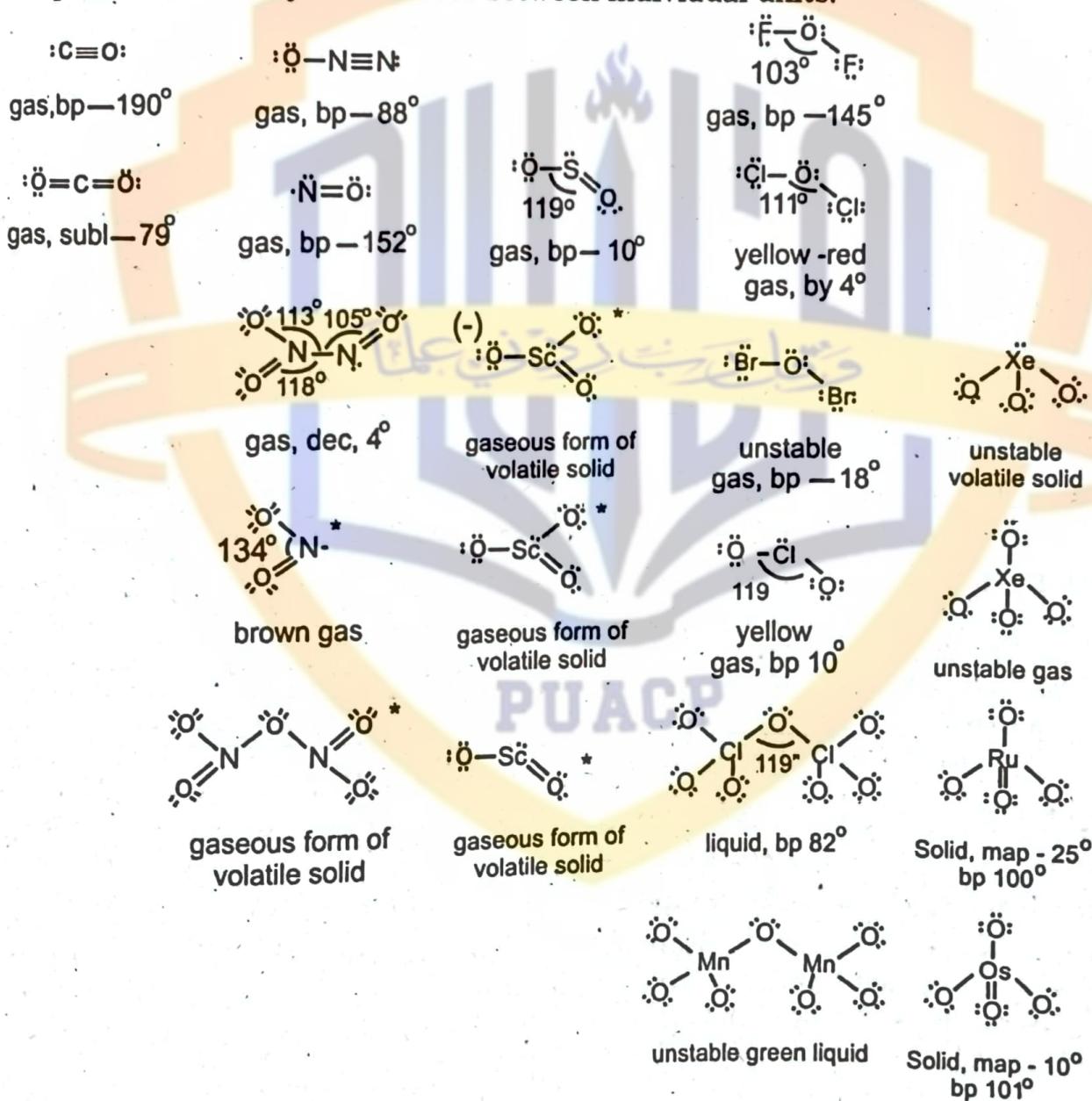
The following trends can be observed:

1. Solids of high m.p are found at the left of the period

2. Moving from left to right, the CN of the more abundant atom (oxygen) declines.
- When CN drops below 2, the melting point drops sharply
3. Small atoms with high oxidation numbers form the oxides with the lowest mp
- 0 gaseous, liquid or low-melting solid structures
4. For metal oxides forming ionic lattices, the melting points and boiling points tend to increase as the charge on the metal increases
- 0 increasing Coulombic forces.

Typical trends in melting or boiling points of oxides in their group oxidation states as the oxidation and group numbers increase are shown in the diagram below:

Monomeric molecules are found in the upper right hand portion of the periodic table and also among the d-block elements with oxidation states of +7 and +8. These species possess relatively weak forces between individual units.



Structures denoted with an asterisk (*) also have alternate oligomeric or polymeric structural forms.

The table below shows important covalent oxides which have polymeric structures.

$(\text{SiO}_2)_x$	$(\text{P}_2\text{O}_5)_x^*$	$(\text{SO}_3)_x^*$	
$\text{CN}(\text{Si}) = 4$	$\text{CN}(\text{P}) = 4$	$\text{CN}(\text{S}) = 4$	
$\text{CN}(\text{O}) = 2$	$\text{CN}(\text{O}) = 1.6$	I-dim	
Solid, mp 1723	Solid	Solid, mp 17	
$(\text{GeO}_2)_x$	$(\text{As}_2\text{O}_5)_x$	$(\text{SeO}_3)_x^*$	
$\text{CN}(\text{Ge}) = 4, 6$	$\text{CN}(\text{As}) = 5$	$\text{CN}(\text{Se}) = 4$	
$\text{CN}(\text{O}) = 2.3$	$\text{CN}(\text{O}) = 2$	$\text{CN}(\text{O}) = 1.33$	
3-dim	3-dim	1-dim	
Solid, mp 1116	Solid, dec 315	Solid, mp 120	
$(\text{SnO}_2)_x$	$(\text{Sb}_2\text{O}_5)_x$	$(\text{TeO}_3)_x$	
$\text{CN}(\text{Sn}) = 6$	$\text{CN}(\text{Sb}) = 6$	$\text{CN}(\text{Te}) = 6$	
$\text{CN}(\text{O}) = 3$	$\text{CN}(\text{O}) = 2.4$	$\text{CN}(\text{O}) = 2$	
3-dim	3-dim	3-dim	
Solid, mp 1127	Solid, dec. 380	Solid, dec 395	
$(\text{PbO}_2)_x$	$(\text{SeO}_2)_x^*$		
$\text{CN}(\text{Pb}) = 6$		$\text{CN}(\text{Se}) = 3 + :$	
$\text{CN}(\text{O}) = 3$		$\text{CN}(\text{O}) = 1.5$	
3-dim		3-dim	
Solid, dec. 290		Solid, mp 315	
$(\text{SnO})_x$	$(\text{Sb}_2\text{O}_3)_x^*$	$(\text{TeO}_2)_x$	(I_2O_5)
$\text{CN}(\text{Sn}) = 4 + :$	$\text{CN}(\text{Sb}) = 3 + :$	$\text{CN}(\text{Te}) = 6 + :$	
$\text{CN}(\text{O}) = 4$	$\text{CN}(\text{O}) = 2$	$\text{CN}(\text{O}) = 3$	
2-dim	2-dim	3-dim	3-dim
Solid, dec. 1080	Solid	Solid, mp 733	Solid, dec 300
$(\text{PbO})_x$	$(\text{Bi}_2\text{O}_3)_x$	$(\text{PoO}_2)_x$	
$\text{CN}(\text{Pb}) = 4 + :$	$\text{CN}(\text{Bi}) = 6 + :$	$\text{CN}(\text{Po}) = 6 + :$	
$\text{CN}(\text{O}) = 4$	$\text{CN}(\text{O}) = 4$	$\text{CN}(\text{O}) = 3$	
2-dim	3-dim	3-dim	
Solid, mp 888	Solid, mp 874	Solid, dec. 500	

Notes: $\text{CN}(\text{Si})$ = average coordination number of silicon 2-dim = forms a two-dimensional or layer polymer mp = melting point dec. = temperature at which the solid decomposes. * = also has monomeric or oligomeric forms: sec. An unshared pair of electrons for the atom in parentheses is indicated by:

Examples of oxides

The oxides of the third row elements are:





Those oxides in the top row are known as the highest oxides of the various elements. These are the oxides where the Period 3 elements are in their highest oxidation states. In these oxides, all the outer electrons in the Period 3 element are being involved in the bonding - from just the one with sodium, to all seven of chlorine's outer electrons.

The structures

The trend in structure is from the metallic oxides containing giant structures of ions on the left of the period via a giant covalent oxide (silicon dioxide) in the middle to molecular oxides on the right.

Melting and boiling points

The giant structures (the metal oxides and silicon dioxide) will have high melting and boiling points because a lot of energy is needed to break the strong bonds (ionic or covalent) operating in three dimensions.

The oxides of phosphorus, sulphur and chlorine consist of individual molecules - some small and simple; others polymeric.

The attractive forces between these molecules will be Van der Waals dispersion and dipole-dipole interactions. These vary in size depending on the size, shape and polarity of the various molecules - but will always be much weaker than the ionic or covalent bonds you need to break in a giant structure.

These oxides tend to be gases, liquids or low melting point solids.

Electrical conductivity

None of these oxides has any free or mobile electrons. That means that none of them will conduct electricity when they are solid.

The ionic oxides can, however, undergo *electrolysis* when they are molten. They can conduct electricity because of the movement of the ions towards the electrodes and the discharge of the ions when they get there.

The metallic oxides

Structures

Sodium, magnesium and aluminum oxides consist of *giant structures containing metal ions and oxide ions*. Magnesium oxide has a structure just like sodium chloride. The other two have more complicated arrangements of the ions beyond the scope of syllabuses at this level (UK A level or its equivalents).

Melting and boiling points

There are strong attractions between the ions in each of these oxides and these attractions need a lot of heat energy to break. These oxides therefore have high melting and boiling points.

Electrical conductivity

None of these conducts electricity in the solid state, but *electrolysis* is possible if they are molten. They conduct electricity because of the movement and discharge of the ions present. The only important example of this is in the electrolysis of aluminum oxide in the manufacture of aluminum.

Whether you can electrolyze molten sodium oxide depends, of course, on whether it actually melts instead of subliming or decomposing under ordinary circumstances. If it sublimes, you won't get any liquid to electrolyze!

Magnesium and aluminum oxides have melting points far too high to be able to electrolyze them in a simple lab.

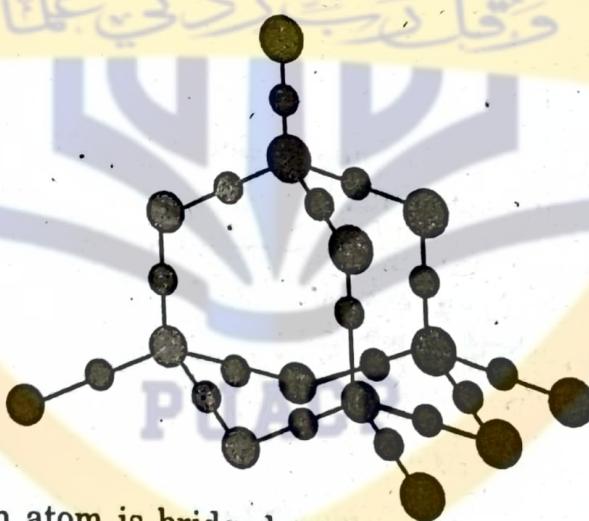
Silicon dioxide (silicon(IV) oxide)

The structure

The electronegativity of the elements increases as you go across the period, and by the time you get to silicon, there isn't enough electronegativity difference between the silicon and the oxygen to form an ionic bond. Silicon dioxide is a **giant covalent structure**.

There are three different crystal forms of silicon dioxide. The easiest one to remember and draw is based on the diamond structure.

Crystalline silicon has the same structure as diamond. To turn it into silicon dioxide, all you need to do is to modify the silicon structure by including some oxygen atoms.



Notice that each silicon atom is bridged to its neighbors by an oxygen atom. Don't forget that this is just a tiny part of a giant structure extending in all 3 dimensions.

Melting and boiling points

Silicon dioxide has a high melting point - varying depending on what the particular structure is (remember that the structure given is only one of three possible structures), but they are all around 1700°C. Very strong silicon-oxygen covalent bonds have to be broken throughout the structure before melting occurs. Silicon dioxide boils at 2230°C.

Because you are talking about a different form of bonding, it doesn't make sense to try to compare these values directly with the metallic oxides. What you can safely say

is that because the metallic oxides and silicon dioxide have giant structures, the melting and boiling points are all high.

Electrical conductivity

Silicon dioxide doesn't have any mobile electrons or ions - so it doesn't conduct electricity either as a solid or a liquid.

The molecular oxides

Phosphorus, sulfur and chlorine all form oxides which consist of molecules. Some of these molecules are fairly simple - others are polymeric. We are just going to look at some of the simple ones.

Melting and boiling points of these oxides will be much lower than those of the metal oxides or silicon dioxide. The intermolecular forces holding one molecule to its neighbors will be van der Waals dispersion forces or dipole-dipole interactions. The strength of these will vary depending on the size of the molecules.

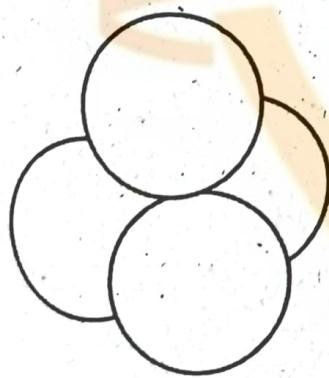
None of these oxides conducts electricity either as solids or as liquids. None of them contains ions or free electrons.

The phosphorus oxides

Phosphorus has two common oxides, phosphorus(III) oxide, P_4O_6 , and phosphorus(V) oxide, P_4O_{10} .

Phosphorus(III) oxide

Phosphorus(III) oxide is a white solid, melting at $24^\circ C$ and boiling at $173^\circ C$. The structure of its molecule is best worked out starting from a P_4 molecule which is a little tetrahedron.

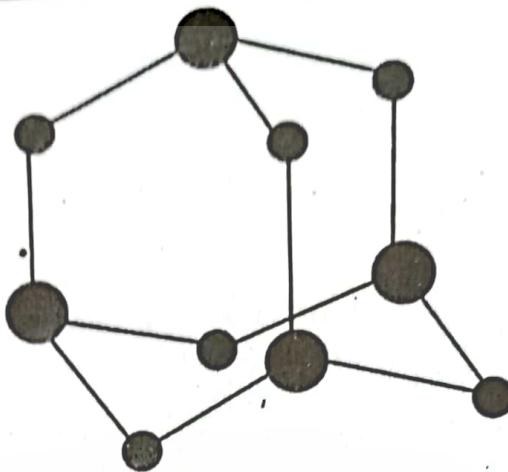


a P_4 molecule



a P_4 molecule

and then replace the bonds by new bonds linking the phosphorus atoms via oxygen atoms. These will be in a V-shape (rather like in water), but you probably wouldn't be penalised if you drew them on a straight line between the phosphorus atoms in an exam.

a $P_4 O_6$ Molecule

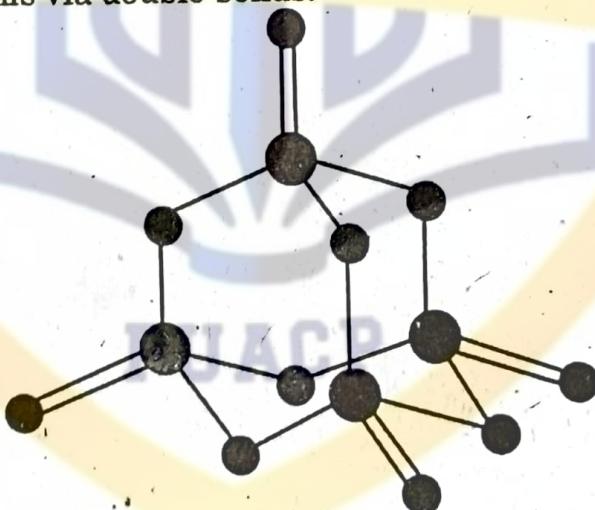
The phosphorus is using only three of its outer electrons (the 3 unpaired p electrons) to form bonds with the oxygens.

Phosphorus(V) oxide

Phosphorus(V) oxide is also a white solid, subliming (turning straight from solid to vapour) at $300^\circ C$. In this case, the phosphorus uses all five of its outer electrons in the bonding.

Solid phosphorus(V) oxide exists in several different forms - some of them polymeric. We are going to concentrate on a simple molecular form, and this is also present in the vapour.

This is most easily drawn starting from P_4O_6 . The other four oxygens are attached to the four phosphorus atoms via double bonds.

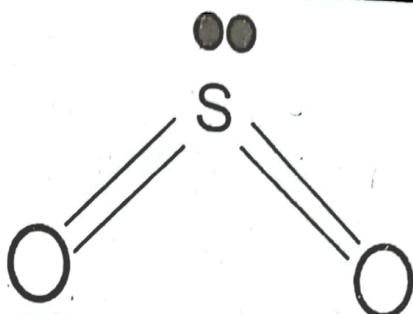
a $P_4 O_{10}$ Molecule

The Sulfur oxides

Sulphur has two common oxides, sulfur dioxide (sulfur(IV) oxide), SO_2 , and sulfur trioxide (sulfur(VI) oxide), SO_3 .

Sulfur dioxide

Sulphur dioxide is a colorless gas at room temperature with an easily recognized choking smell. It consists of simple SO_2 molecules.

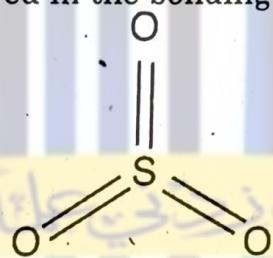


The sulfur uses 4 of its outer electrons to form the double bonds with the oxygen, leaving the other two as a lone pair on the sulfur. The bent shape of SO_2 is due to this lone pair.

Sulfur trioxide

Pure sulfur trioxide is a white solid with a low melting and boiling point. It reacts very rapidly with water vapour in the air to form sulfuric acid. That means that if you make some in the lab, you tend to see it as a white sludge which fumes dramatically in moist air (forming a fog of sulfuric acid droplets).

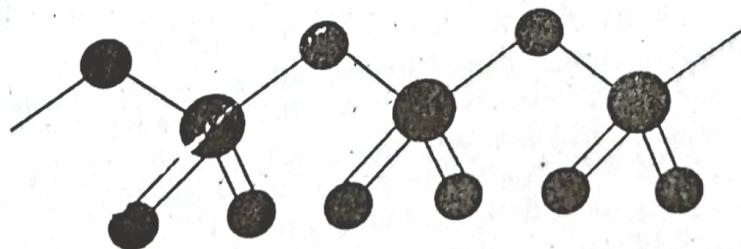
Gaseous sulfur trioxide consists of simple SO_3 molecules in which all six of the sulfur's outer electrons are involved in the bonding.



There are various forms of solid sulfur trioxide. The simplest one is a trimer, S_3O_9 , where three SO_3 molecules are joined up and arranged in a ring.



There are also other polymeric forms in which the SO_3 molecules join together in long chains. For example:



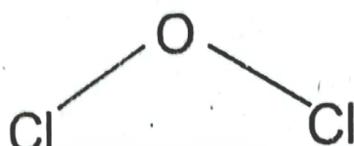
The fact that the simple molecules join up in this way to make bigger structures is what makes the sulfur trioxide a solid rather than a gas.

The chlorine oxides

The chlorine oxides
 Chlorine forms several oxides. Here we are just looking at two of them (the only ones mentioned by any of the UK syllabuses) - chlorine(I) oxide, Cl_2O , and chlorine(VII) oxide, Cl_2O_7 .

Chlorine(I) oxide

Chlorine(I) oxide
Chlorine(I) oxide is a yellowish-red gas at room temperature. It consists of simple small molecules.



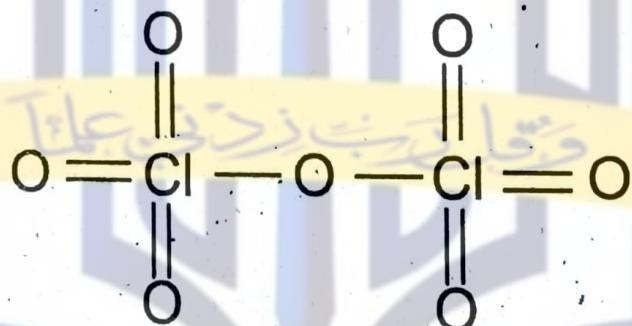
There's nothing in the least surprising about this molecule and it's physical properties are just what you would expect for a molecule this size.

Chlorine(VII) oxide

In chlorine(VII) oxide, the chlorine uses all of its seven outer electrons in bonds with oxygen. This produces a much bigger molecule, and so you would expect its melting point and boiling point to be higher than chlorine(I) oxide.

Chlorine(VII) oxide is a colourless oily liquid at room temperature.

In the diagram, for simplicity I have drawn a standard structural formula. In fact, the shape is tetrahedral around both chlorines, and V-shaped around the central oxygen.



19.4 STRUCTURES OF SOME BINARY AND TERNARY METAL OXIDES

Oxides have a range of different structures, from individual molecules to polymeric and crystalline structures. At standard conditions, oxides may range from solids to gases. Metal oxides have variety of complex structures, especially in mixed metal oxides, such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, layer lattices - CDI_2 , BIL_3 ; REO_3 , Mn_2O_3 , Corundum, Perovskite, Ilmenite and Calcite.

The oxide minerals typically present in soils comprise oxides, hydroxides, oxyhydroxides, and hydrated oxides of Si, Fe, Mn, Al, and Ti. With the exception of the Si oxide quartz and some Ti oxides, which are predominantly inherited from primary (rock) minerals, most oxides form in soil. The metal cations Fe^{2+} , Mn^{2+} , Ti^{4+} , Al^{3+} , and Si^{4+} are released from silicates by weathering. The divalent cations Mn and Fe oxidize and hydrolyze, and precipitate almost exclusively as oxide minerals. Al^{3+} and Si^{4+} have a strong tendency to form secondary aluminosilicate clay minerals; the formation of Al and Si oxides requires special conditions. All oxides have a very low solubility at common soil pH and are therefore enriched during pedogenesis. Highly weathered soils, which have lost a substantial part of their alkalis, alkaline earths, and Si, may contain as much as 50% wt metal oxides.

Oxides of Fe, Mn, and Al may exhibit a high surface area, with reactive surface sites which strongly bind oxyanions and metal cations, thereby impacting the availability and mobility of plant nutrients and toxic metals. Some Mn oxides have a strong oxidizing power and may degrade organic pesticides, decrease or increase the toxicity of heavy metals, and contribute to the formation of soil organic matter. In contrast, sand-sized crystals of the Si oxide quartz are chemically very inert.

The basic structural unit of Fe, Mn, Al, and Ti oxides are cationic metal centers bound to six oxygens. If one drastically reduces the size of the oxygens in relation to the metal cations, this arrangement can be visualized as an octahedron (Figure 19.1). The octahedral may be linked to each other in three ways, sharing oxygen corners (1 O), sharing edges (2 O), or faces (3 O). Many oxide minerals such as goethite contain only the first two types of connections, while the Fe oxide hematite contains all three. Silicon is bound to four oxygens, forming a tetrahedron. These tetrahedral are connected via corners only. We will use this polyhedral approach in the text and in figures to introduce the mineral species and highlight their major differences and similarities. For each oxide group, we will give an overview including general formation pathways and influence on soil properties. This overview is followed by a description of the minerals, their occurrence in soil, and specific conditions of their formation.

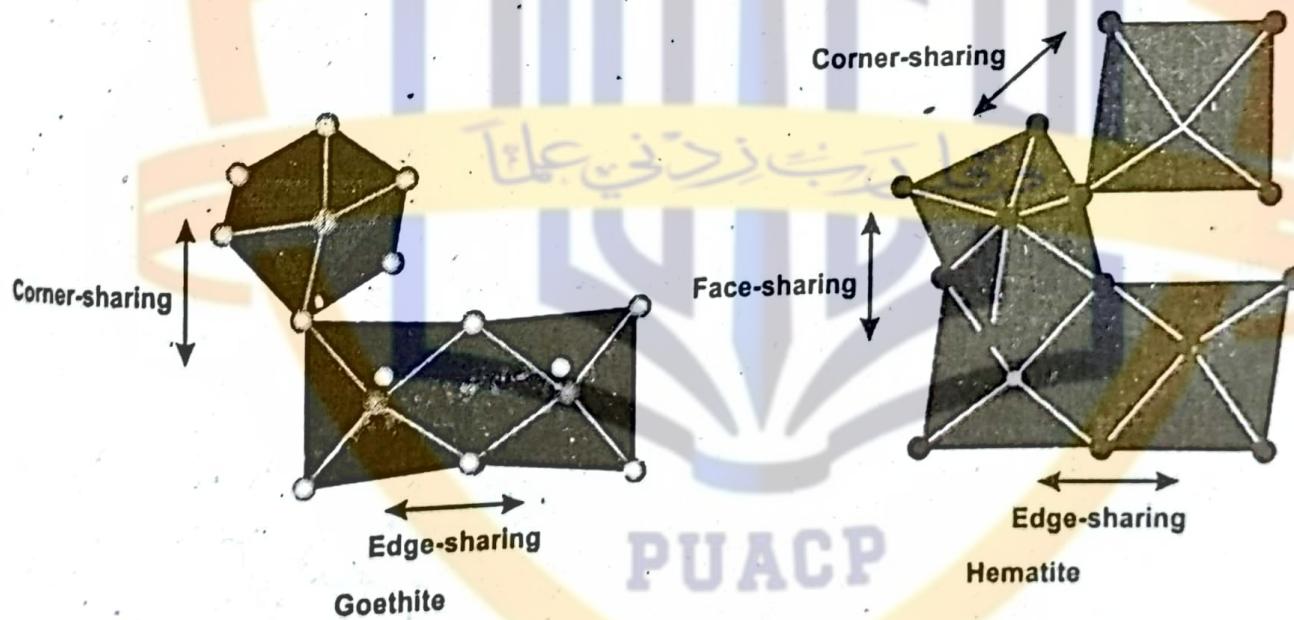


Figure 19.1: Goethite and Hematite

The structure of crystalline compounds can be understood only after knowing the close packing of solid spheres as all the constituent particles (whether they are atoms, ions or molecules) may be treated as somewhat more or less spherical in shape.

The problem of spheres packed closely was first studied in a mathematical framework by Thomas Harriot in 158. The idea was initiated by a question on piling the cannonballs on ships, and the question was posed to T. Harriot by Sir W. Raleigh when they were on their expedition to the land of America. The usual scheme of piling the cannonballs included the placement in a triangular or rectangular wooden frame, which forms a three or four-sided pyramidal shape. Both arrangements produce a face-centered cubic (fcc) lattice with different orientations to the base.

However, the hexagonal-close-packing (hcp) scheme would result in a six-sided pyramidal shape with a hexagonal base. These two simple regular lattices achieve the highest average density and are based upon sheets of spheres placed at the vertices trigonal with a tiling pattern. However, they vary in the stacked style of these sheets.

The packing of identical spheres in tow dimensions can be visualized in two arrangements as given below.

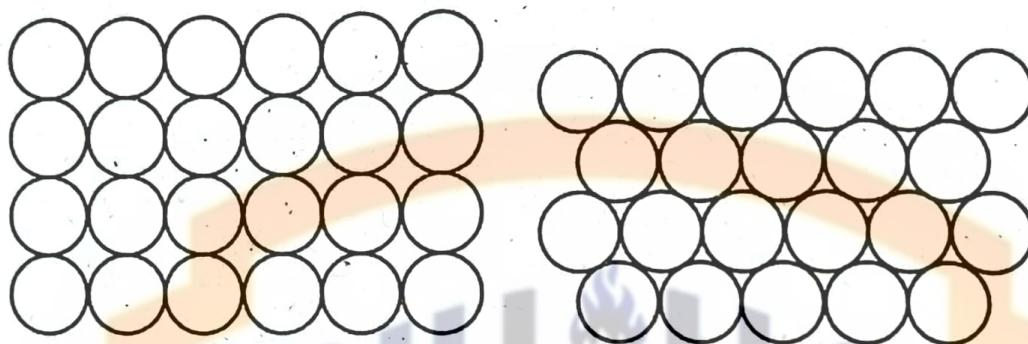


Figure 19.2. The close packing of identical spheres in two dimensions.

It has been observed that 52.4% of available space is occupied in the arrangement I while 60.4% of available space is occupied in arrangement II. The remaining space is empty and is labeled as void volume. Hence, the arrangement II has greater efficiency than arrangement I. Furthermore, it can be noticed that the coordination number of each sphere in arrangement II is six but four in case of arrangement I and the lines joining the centers of nearest spheres in the arrangement I form a square but a triangle in arrangement II.

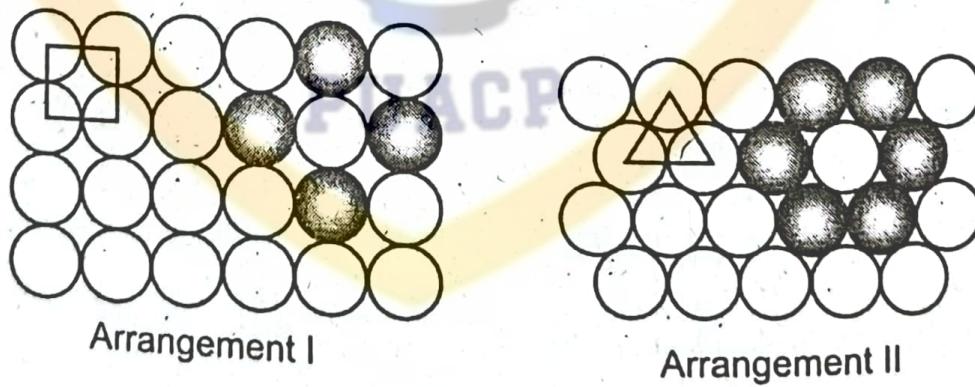


Figure 19.3. The coordination number and nearest sphere system in close packing of identical spheres in two dimensions.

The two-dimensional packing can successfully be extended to three-dimensional packing can successfully be extended to three-dimensional packing just

by placing the other layers of packed identical spheres over it. This can be achieved in two ways as depicted below.

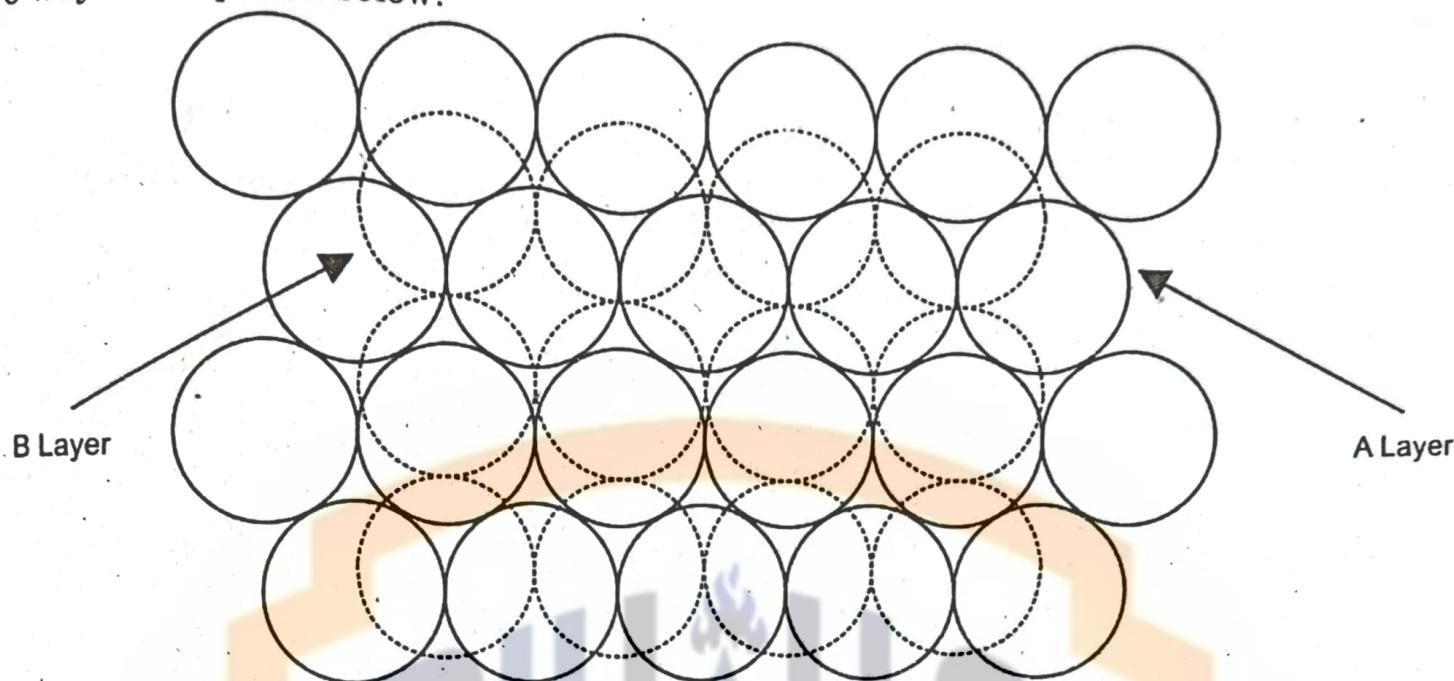


Figure 19.4. The extension of close packing of identical sphere systems in two dimensions to three dimensions.

The first layer is labeled as A, while the second layer B is placed over the first layer in such a way that its spheres are covering the b-voids. Now, if we create a third layer directly over the layer A, then the hcp lattice is formed and if the third layer is placed over a-voids in the first layer, then the fcc lattice is built. In both the arrangements, the fcc as well as hcp, each sphere has twelve neighboring spheres. For every sphere, there is one void surrounded by six neighboring spheres (octahedral site) and two smaller voids surrounded by four neighboring spheres (tetrahedral site). The distances to the centers of these gaps from the centers of the surrounding spheres are for the tetrahedral, and $\sqrt{3}/2$ for the tetrahedral, and $\sqrt{2}$ for the octahedral when the sphere radius is unity.

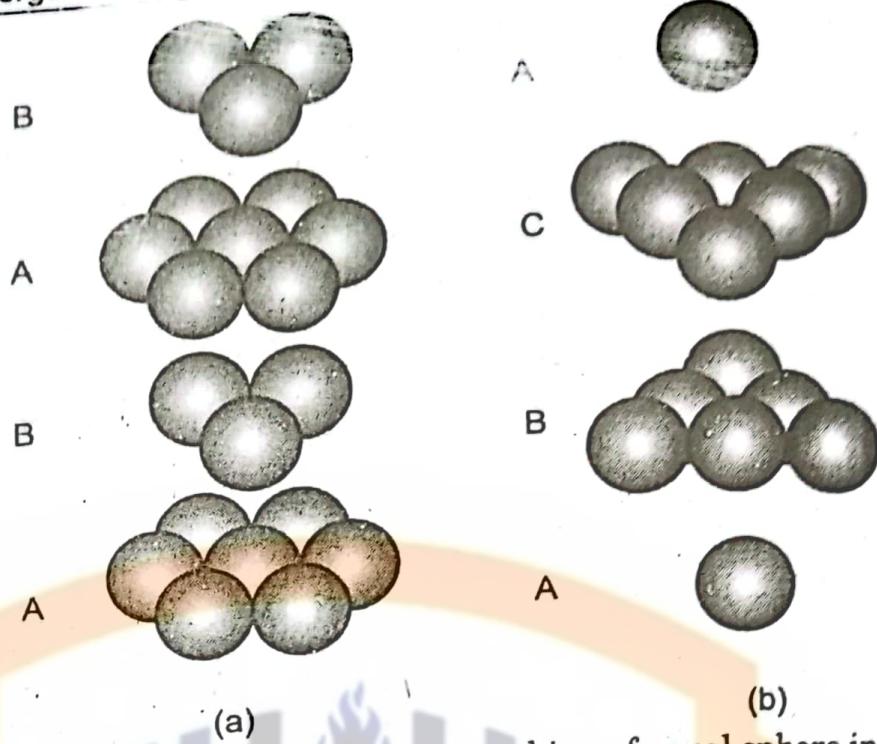


Figure 19.5. The illustration of the close-packing of equal sphere in both (a) hcp and (b) fcc lattices.

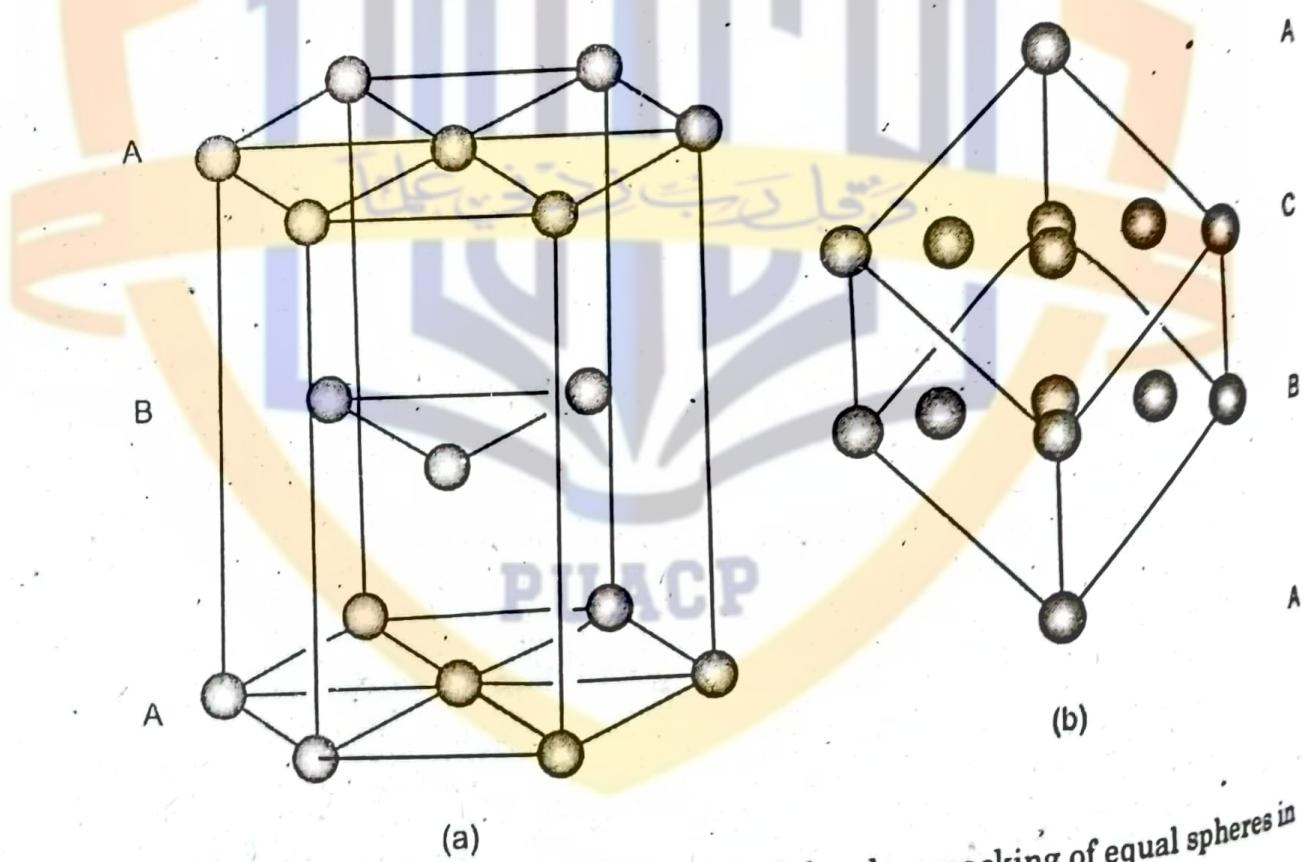


Figure 19.6. The balls and stick model of the close-packing of equal spheres in both (a) hcp and (b) fcc lattices.

The number of interstitial sites, tetrahedral as well as octahedral, is the same for fcc and hcp lattice systems. However, the tetrahedral sites are double in number than octahedral ones. A number of crystal structures are obtained by the close-packing of one kind of atom, or by a close-packing of bigger ions having smaller ions obtained by the close-packing of one kind of atom, or by a close-packing of bigger ions having smaller ions occupying the void spaces. The hexagonal and cubic patterns of

packing are quite close to each other in energy, and therefore, it might be problematic to predict the form preferred using first-principle calculations.

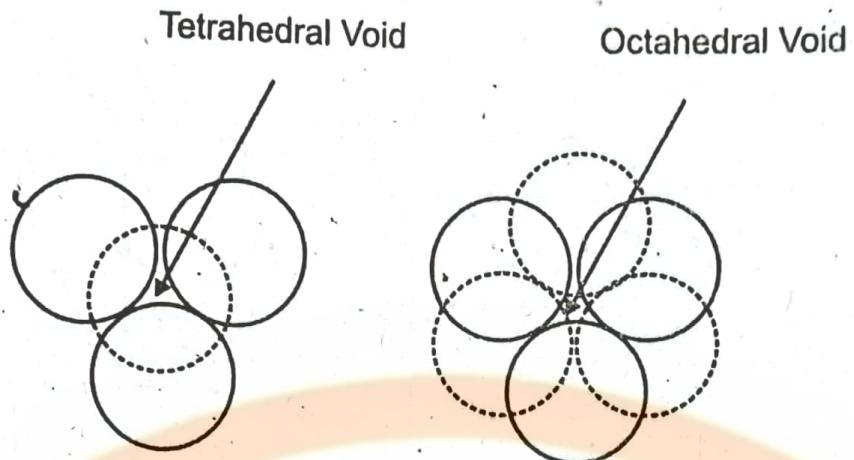


Figure 19.7. The formation of a tetrahedral and octahedral void in close packing of identical spheres in three dimensions.

The location of interstitial sites in hexagonal close-packing and cubic close packing is quite important as it is expected to be occupied by smaller ion which is generally cation. Nonetheless, the anions can also occupy these tetrahedral octahedral voids if they are smaller in size.

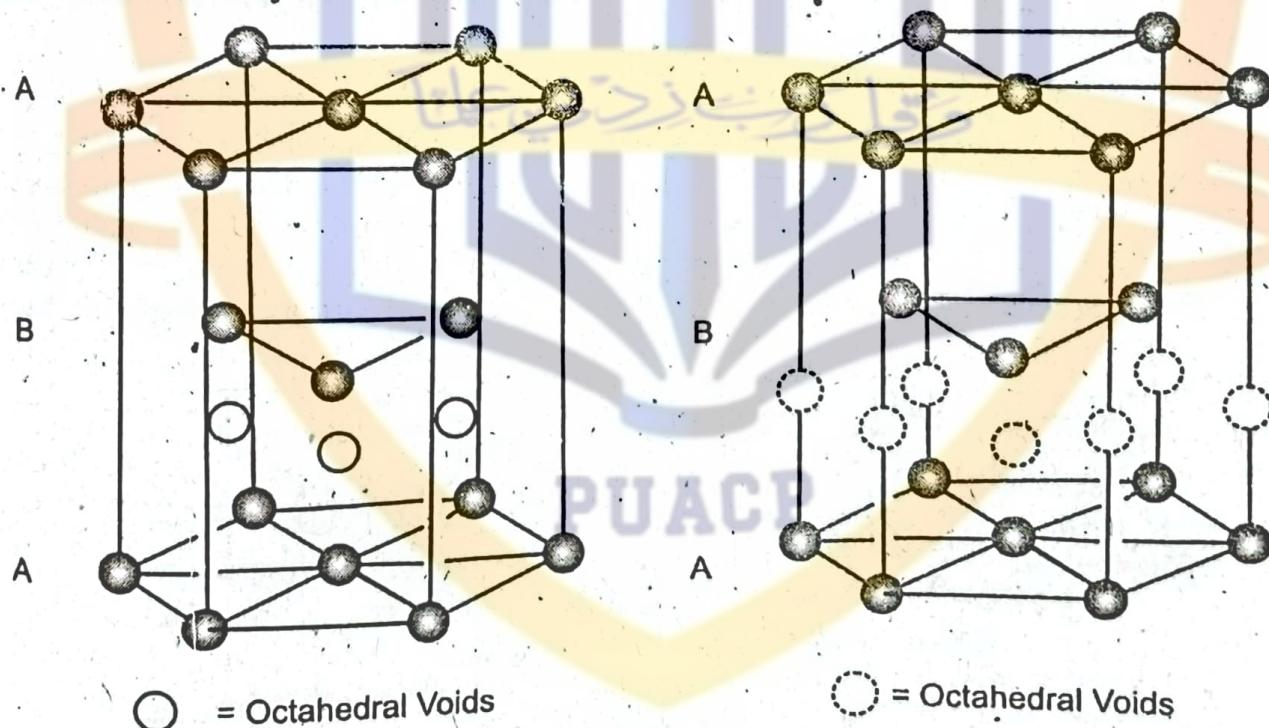


Figure 19.8. The location of octahedral and tetrahedral sites in hexagonal close packing or hcp lattices formed by the identical sphere.

In a hcp structure, the arrangement of the third layer is the same as the spheres' placement of first layer and covers all the tetrahedral voids. The hcp and fcc type packings of equal spheres are of the highest density with the highest symmetry. Though, the denser packings are known; they, however, involve spheres of unequal

size. Only a packing of non-spherical shapes, like honeycombs, is capable of occupying a hundred percent space.

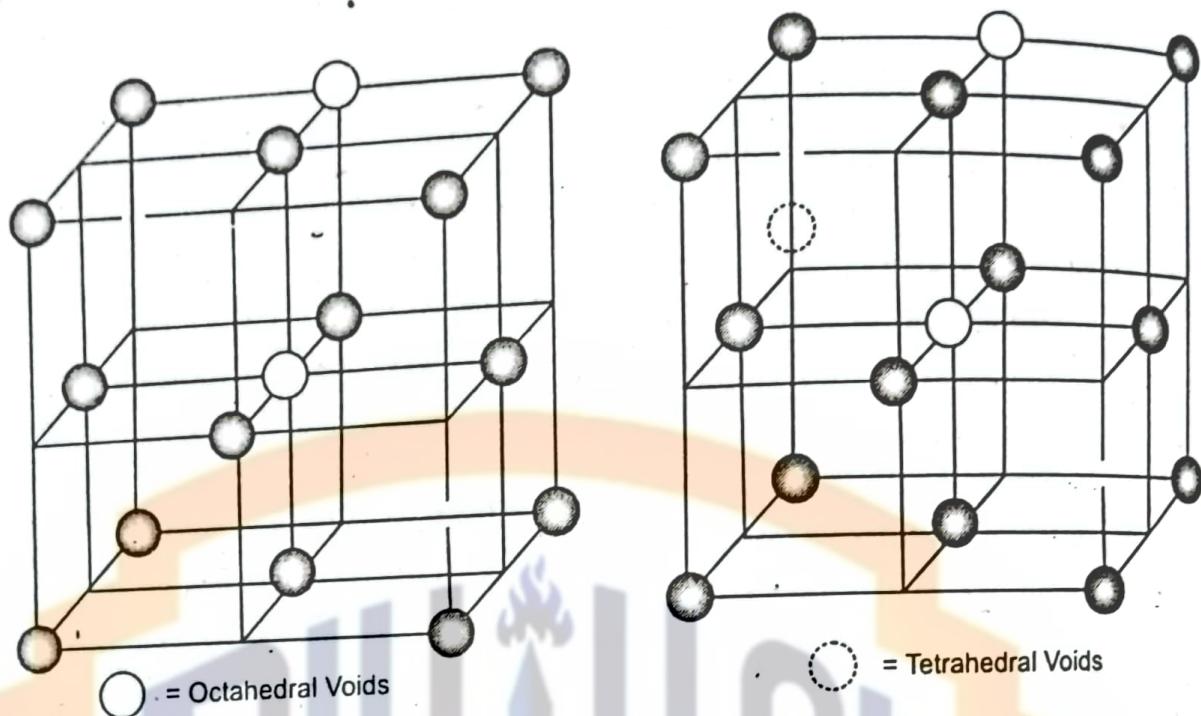


Figure 19.9. The location of octahedral and tetrahedral sites in cubic close packing or fcc lattices.

In addition to the hcp and fcc arrangements, one more common lattice-type also exists, called as body-centered cubic or simply the bcc lattice. The placement of the second layer opens the spheres of the first layer and the third layer is exactly eclipsed to the first layer. Each sphere is in contact with spheres of the first layer and four spheres of the third layer giving an overall coordination number of eight.

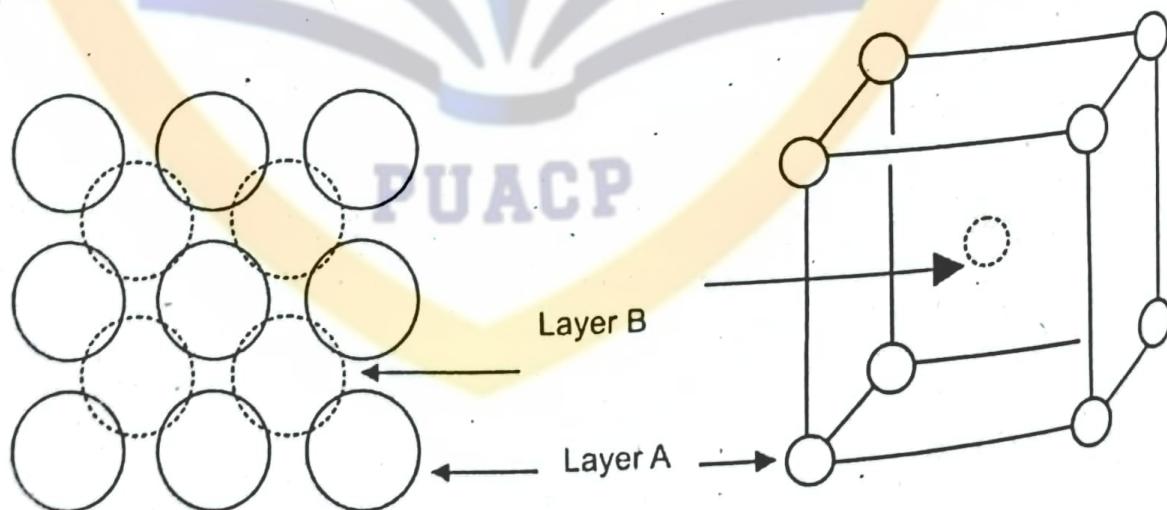


Figure 19.10. Body-centered close packing of equal spheres.

This arrangement can also be visualized as a derivative of a simple cubic unit cell in which eight spheres are present at the corners of the cube and one extra sphere is placed in the center. The packing efficiency of body-centered cubic packing is lesser

than hcp or fcc lattice system and only 68% of the available volume is actually occupied.

Now, as we have studied the packing of equal spheres and the resulting void types, we are ready to discuss the crystal structure of some important binary and ternary compounds.

➤ Antifluorite (Na_2O)

It is the mineral form of sodium oxide, the unit cell of antifluorite lattice is shown below.

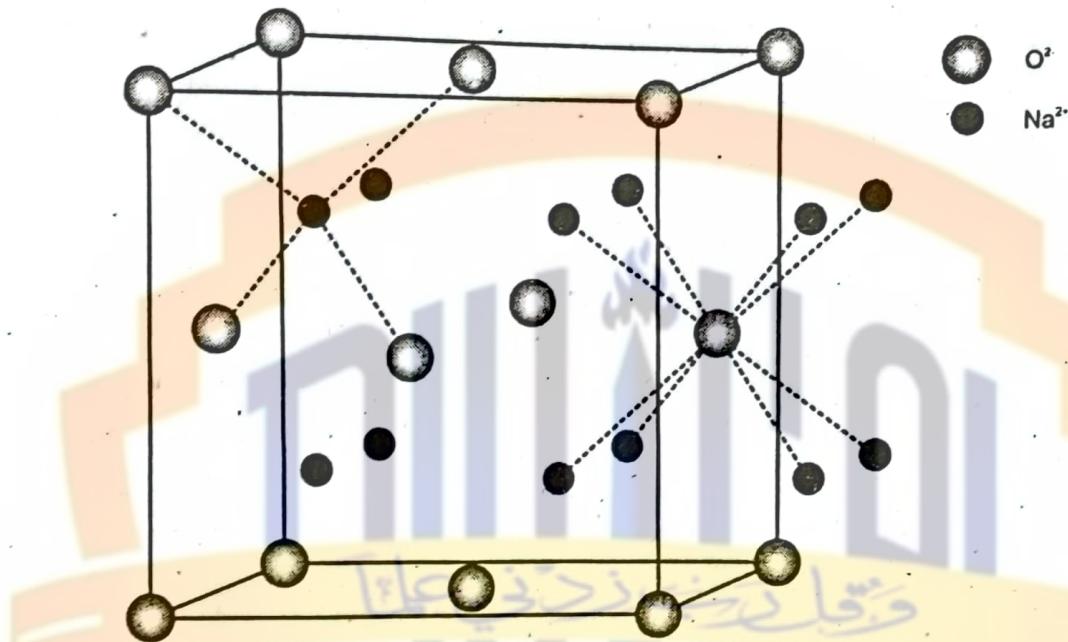


Figure 19.11. The crystal structure of calcium fluoride Na_2O .

The main features of this crystal structure are as follow:

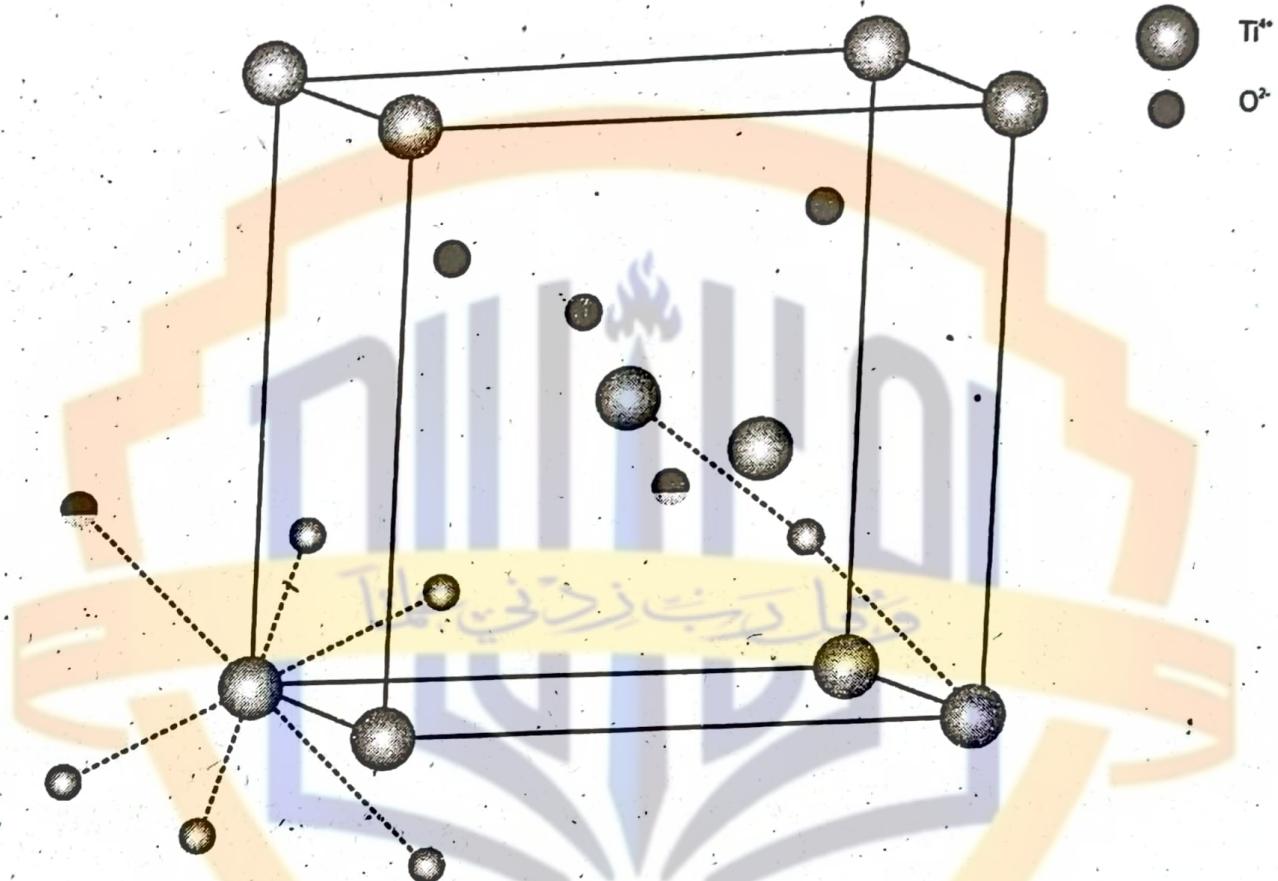
1. The O^{2-} ions are present in cubic close packing or fcc lattice in which they are present at all the corners and at the center of each face.
2. The Na^+ ions are occupying all the tetrahedral sites.
3. The number of tetrahedral sites for the CCP packing of N spheres is $2N$. This means that two tetrahedral sites are formed for each O^{2-} ion. Now, because all the tetrahedral sites are occupied by Na^+ anions, the stoichiometry of the compound becomes 2:1.
4. The coordination number of O^{2-} is eight while each Na^+ ion is surrounded by four oxide ions. The surrounding geometry of O^{2-} ion is tetrahedral and of Na^+ is cubical in nature. Therefore, the coordination number ratio of O^{2-} and Na^+ is 4:8.

The other examples of this type of structure are Li_2O , K_2O , Rb_2O . It is worth noting that in this motif the positions of the anions and cations are reversed relative to their positions in CaF_2 , with sodium ions tetrahedrally coordinated to 4 oxide ions and oxide cubically coordinated to 8 sodium ions. The Na_2O is a primary component of windows and glasses though it is added

in the form of "soda" (Na_2CO_3). The Na_2O does not exist in glasses explicitly since glasses are cross-linked polymers of complex profile. The Na_2CO_3 also serves as a flux to lower the temperature for melting the silica. The melting temperature of soda glass is much lower than pure silica but has a slightly higher value of elasticity.

➤ **Rutile (TiO_2)**

It is the mineral form of titanium oxide, TiO_2 . The unit cell of titanium oxide is shown below.



Structure of Rutile (TiO_2)

Figure 19.12. The crystal structure of rutile or TiO_2 .

The main features of this crystal structure are as follows:

1. The Ti^{4+} ions are present in distorted body-centered cubic close packing in which they are present at all the corners and at the center of the distorted cube. The unit cell cannot be labeled as cubic because all the three sides are not equal to each other. One of the edges is different from the other two. Hence, the structure is described as tetragonal in nature.
2. The Ti^{4+} ions are surrounded by six O^{2-} ions while each oxide ion is surrounded by three Ti^{4+} ions. Occupying all the tetrahedral sites. The coordinating geometry of Ti^{4+} ion is octahedral and of O^{2-} is trigonal in nature. Therefore, the coordination number ratio of Ti^{4+} and O^{2-} is 6:3.

The refractive index of rutile at visible wavelengths is highest than any known crystal, and also shows a particularly high dispersion and large

birefringence. These properties make it useful for the manufacturing of some particular optical elements like polarization optics for longer visible and infrared radiations. Now because the rutile is also a large band-gap semiconductor, it has been in the limelight for the research area of finding its applications as a functional oxide for dilute magnetism and photocatalysis.

➤ Cristobalite (SiO_2) :

The mineral cristobalite has the same structural formula to quartz i.e. SiO_2 , but a different crystal structure. The cristobalite phase is stable above 1470°C (β -Cristobalite), but can also be crystallized metastable at lower temperatures in α -Cristobalite. The crystal structure of the two forms can be discussed as:

1. β -Cristobalite: The unit cell of this high-temperature form is shown below.

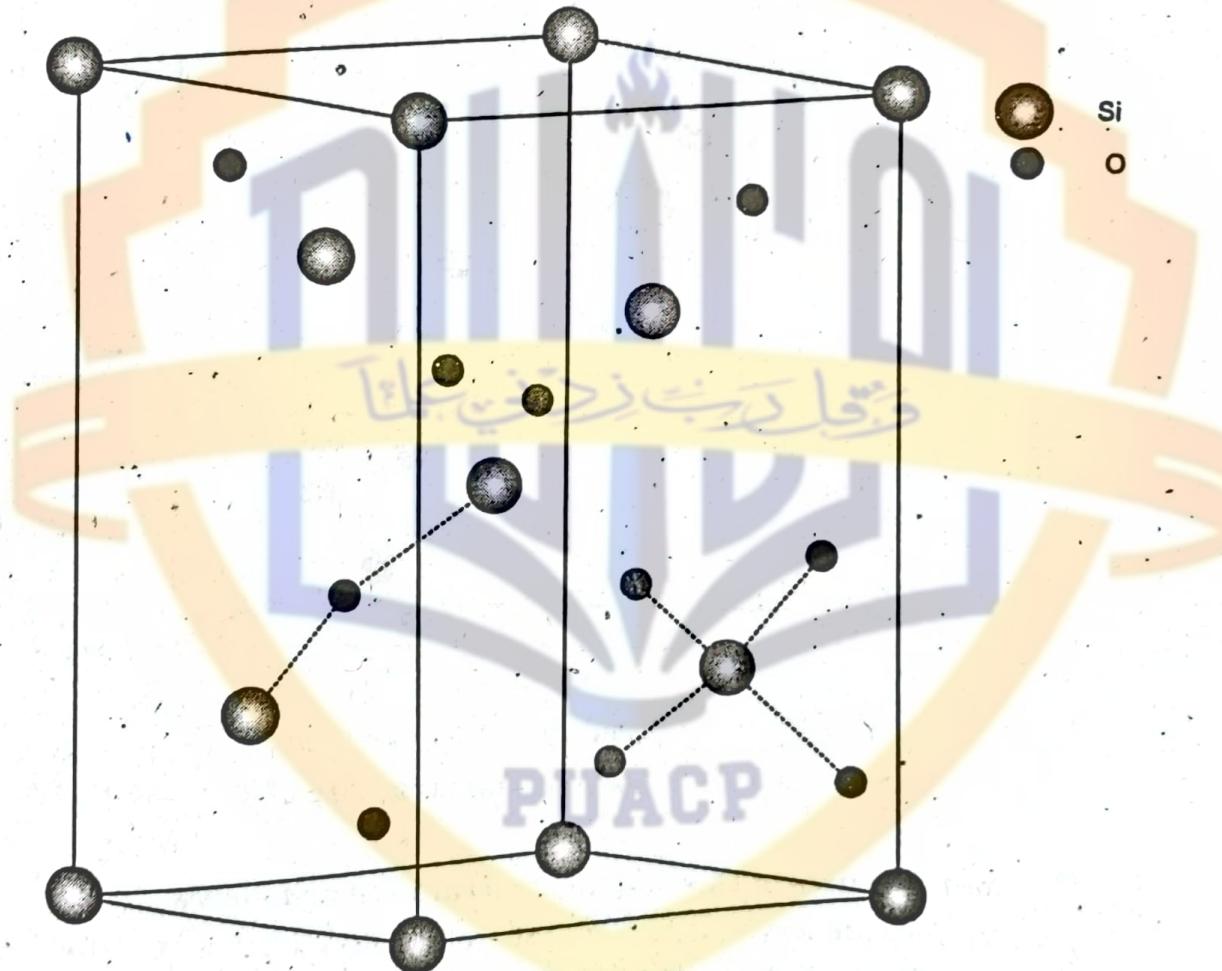


Figure 19.13. The crystal structure of β -Cristobalite.

1. The main features of this crystal structure are as follows:

β -cristobalite crystallizes in the tetragonal lattice in which silicon atoms are present at all the corners and at four faces unit cell.

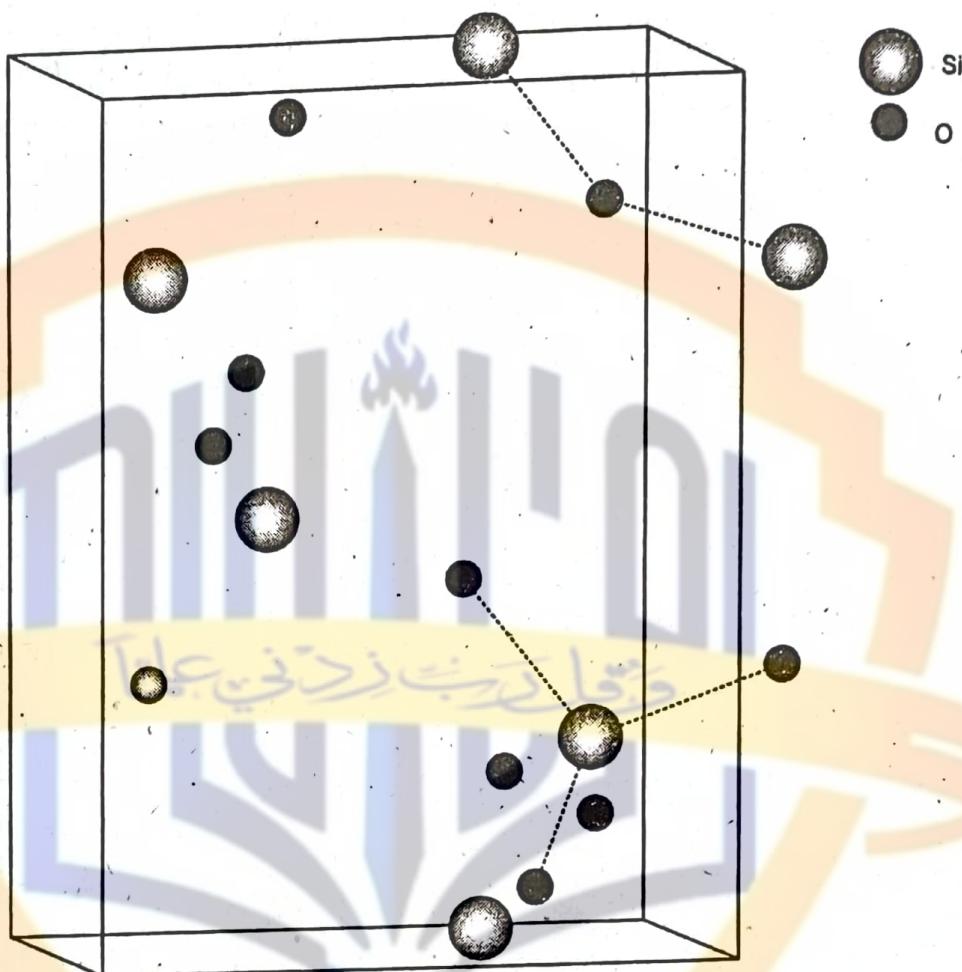
2. The oxygen atoms are surrounded by two silicon atoms while each silicon atom is coordinated by four oxygen atoms. The coordinating geometry of

silicon ion is tetrahedral and of oxygen is V-shaped in nature. Therefore, the coordination number ratio of Si and O is 4:2.

3. The number of formula units present per unit cell is 4.

Cristobalite is found as white spherulites or octahedral in acidic volcanic rocks and in converted diatomaceous deposits in California.

2. α -Cristobalite: The unit cell of this high-temperature form is shown below.



Structure of α -Cristobalite

Figure 19.14. The crystal structure of α -cristobalite.

The main features of this crystal structure are as follows:

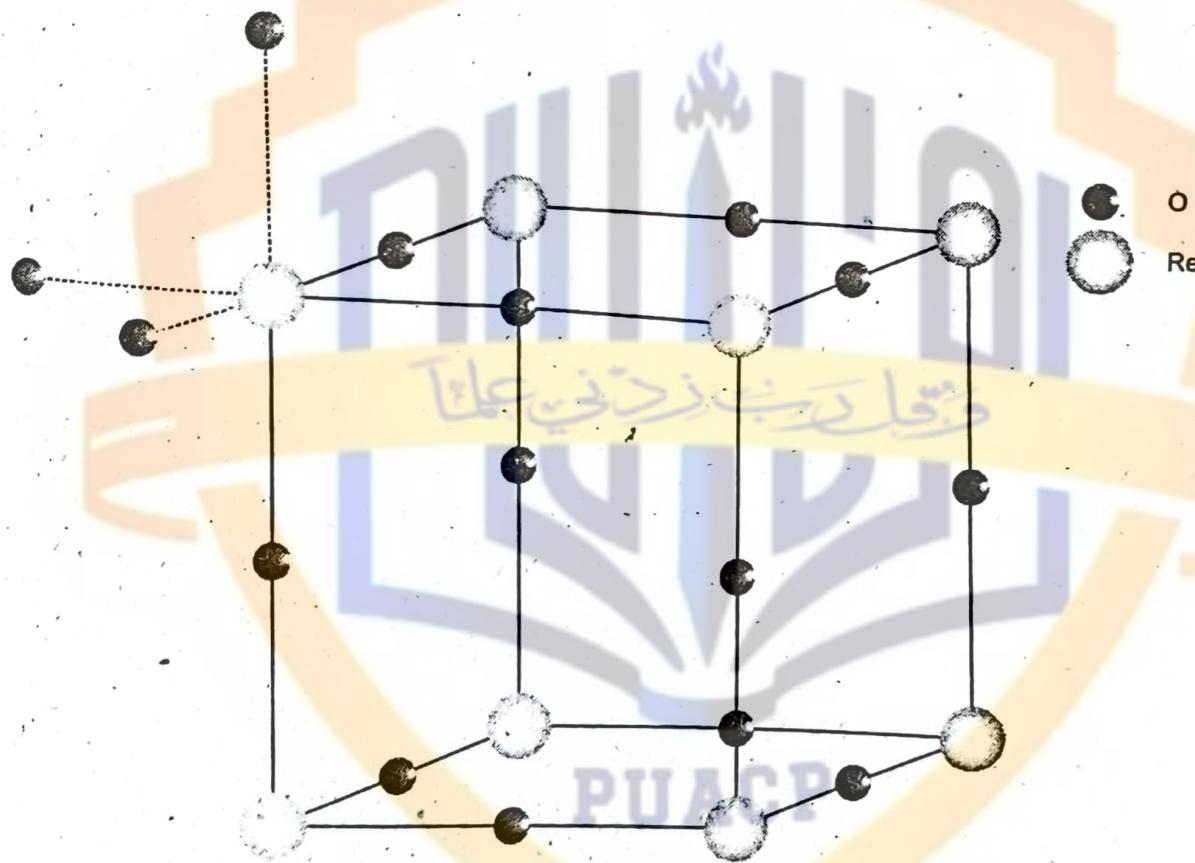
1. α -cristobalite crystallized in the tetragonal lattice in which three silicon atoms are present inside while two silicon atoms are situated at two opposite faces unit cell.
2. The oxygen atoms are surrounded by two silicon atoms while each silicon atom is coordinated by four oxygen atoms. The coordinating geometry of silicon ion is tetrahedral and of oxygen is V-shaped in nature. Therefore, the coordination number ratio of Si and O is 4:2.
3. Like β -cristobalite, the number of formula units presents per unit cell is also

The high temperatures α -cristobalite form transforms into β -cristobalite if it is cooled below 250°C at ambient pressure. This transition is variously called the low-

high or $\alpha - \beta$ transition. In the transitioning $\alpha - \beta$ transition. In the transitioning $\alpha - \beta$ phase, only one of the three degenerate cubic crystallographic axes preserve a 4-fold axis of rotation in the tetragonal phase. Moreover, various twins can form within the same grain due to the arbitrary choice of axis. The coupling of discontinues nature of the transition with different twin orientations can cause significant mechanical damage to the substance in which the cristobalite phase is present and that pass recurrently through the transition temperature.

➤ ReO_3

The rhenium oxide or ReO_3 is a reddish inorganic solid with a metallic luster, which looks like copper. It is the only trioxide of group seven which is stable. The unit cell of ReO_3 is shown below.



Unit Cell of ReO_3

Figure 19.15. The unit cell of ReO_3 crystal system.

- The main features of this crystal structure are as follows:
1. Rhenium oxide crystallized with a primitive cubic unit cell. Re atoms are present at all the corners while the oxygen atoms are situated center of at all the edges.
 2. Each Re atom is surrounded by six oxygen atoms while each O atom is coordinated by two rhenium atoms. The coordinating geometry of rhenium

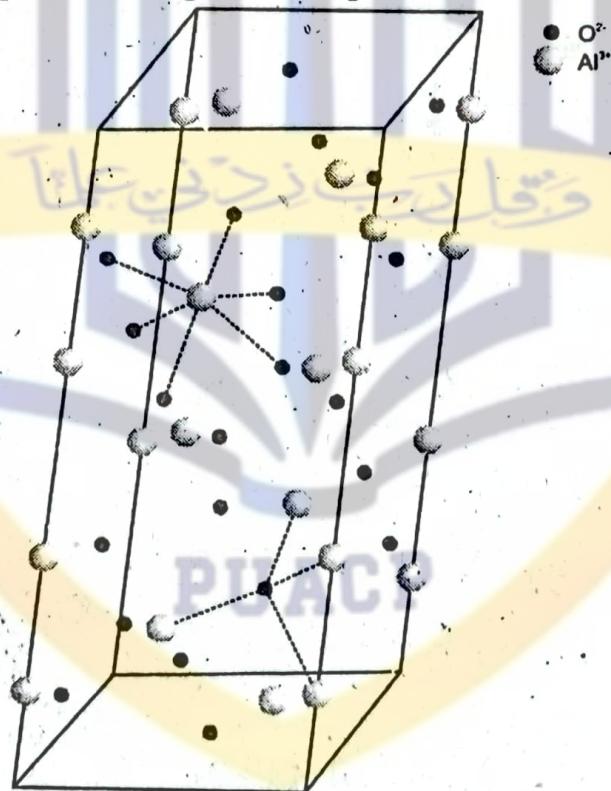
atom is octahedral and of oxygen atom is linear in nature. Therefore, the coordination number ratio of Re and O is 6:2.

3. The number of formula units present per unit cell is one.
4. The octahedron units, ReO_6 , share corners to form the 3-dimensional structure.
5. The ReO_3 is similar to perovskite (ABO_3), just large A cation absent at the unit-cell center.

Rhenium trioxide finds some use in organic synthesis as a catalyst for amide reduction. Rhenium trioxide (ReO_3) is a thermally stable but highly insoluble substance that is quite suitable for optic, glass and ceramic based other devices.

➤ Corundum

Corundum is a crystalline state of Al_2O_3 typically having traces of titanium, vanadium, iron, and chromium in general. The corundum is a rock-forming mineral. It is a transparent material naturally but can show many colors when the impurities are present. The transparent specimens are used as gems, called padparadscha if pink-orange and ruby if red; while the remaining colors are called sapphire in common, e.g., green sapphire for a greenish specimen.



Unit Cell of $\alpha\text{-Al}_2\text{O}_3$

Figure 19.16. The unit cell of $\alpha\text{-Al}_2\text{O}_3$ crystal system.

The main features of this crystal structure are as follows:

1. $\alpha\text{-Al}_2\text{O}_3$ crystallizes in the trigonal lattice in which oxide ions form a slightly distorted hcp, in which two-thirds of the voids between the octahedral sites are occupied by aluminum ions.

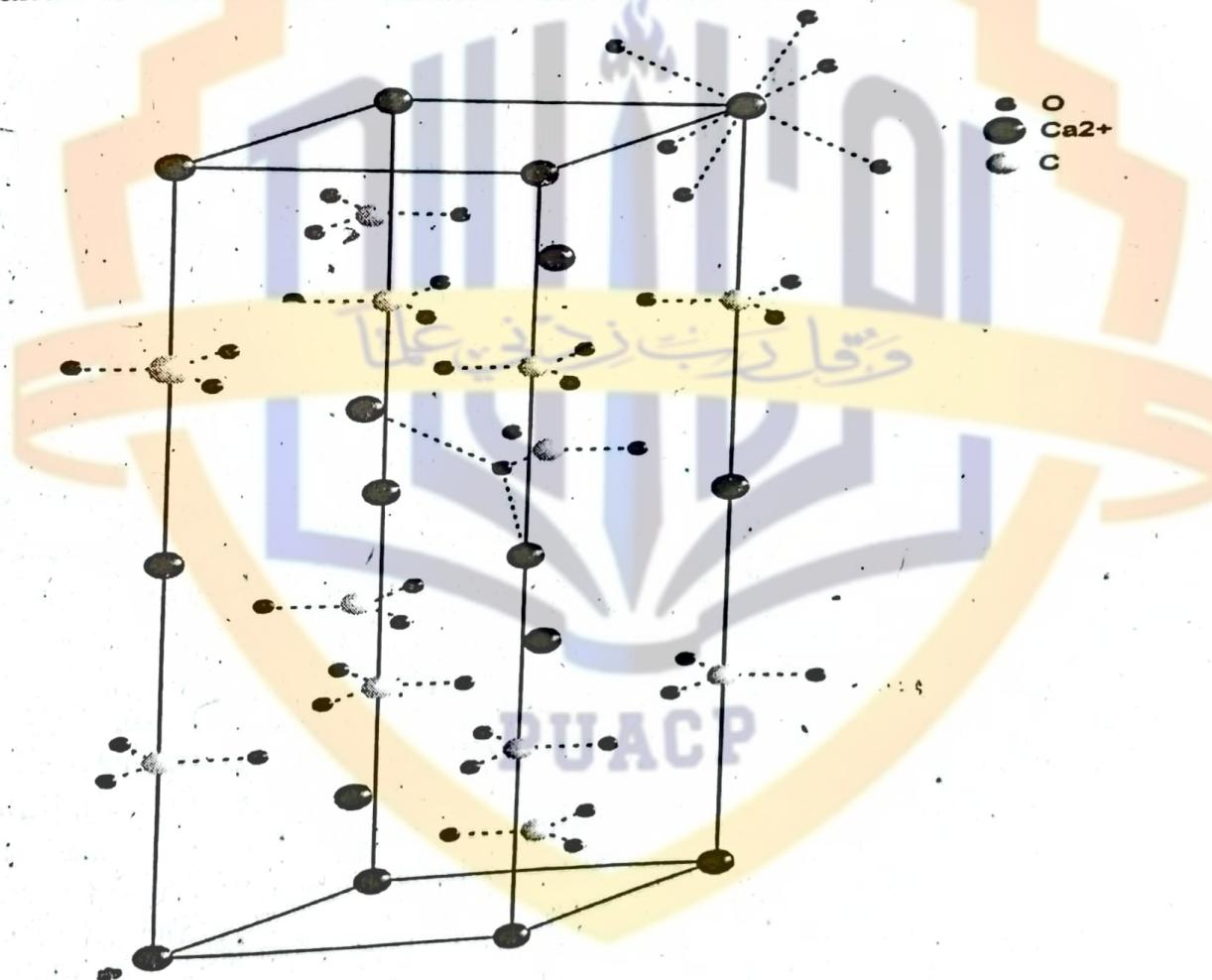
2. Each Al^{3+} ion is surrounded by six oxide ions while each O^{2-} ion is coordinated by four aluminum ions. The coordinating geometry of Al^{3+} is distorted octahedral and of oxide, the ion is distorted tetrahedral in nature. Therefore, the coordination number ratio of Al^{3+} and O^{2-} is 6:4.

3. The number of formula units present per unit cell is six.

Besides its use as a valuable gem, corundum mineral also finds some use as an abrasive due to the extreme hardness of the material (9 on Mohs hardness scale). It is used for grinding optical glass and for polishing metals and has also been made into sandpapers and grinding wheels.

➤ Calcite

The carbonate mineral calcite is the most stable polymorph of CaCO_3 (calcium carbonate). The word calcite is a derivative of German word calcite, a term coined in the nineteenth century from the Latin for lime, and the suffix -ite for minerals. The unit cell is shown below.



Unit Cell of Calcite (CaCO_3)

Figure 19.17. The unit cell of calcite crystal.

The main features of this crystal structure are as follows:

CaCO_3 crystallizes in a trigonal (hexagonal) crystal system in which layers of Ca^{2+} metal ions are in alternation with stacks of carbonate layers. The carbonate layers are made-up of flat triangular-shaped CO_3^{2-} ions, with a central carbon surrounded by three oxygens at each corner of a triangle. This triangular

structural unit is the key component in the trigonal symmetry of this mineral group.

2. Each Ca^{2+} ion is surrounded by six oxygen atoms while the carbon atom of carbonate ion is coordinated by the oxygens in a trigonal fashion. However, each oxygen is coordinated by two Ca^{2+} ions and one C atom. The coordinating geometry of calcium ion is octahedral and of carbon is trigonal in nature. Hence, the coordination number ratio of Ca^{2+} , C and O ions is 6:3:3.

The optical calcite of very high-grade was used in the second world war (WWII) for gun sights, specifically in bomb sights and anti-aircraft artillery. Also, various experimental studies have been carried out to use calcite for a cloak of invisibility. The calcite precipitated microbiologically, has a wide range of applications, like soil-stabilization, soil remediation and concrete repair. Calcite, obtained from an 80-kg sample of Carrara marble, is used as the IAEA-603 isotopic standard in mass spectrometry for the calibration of C^{13} and O^{18} .

➤ Perovskites

It is a calcium titanium oxide mineral composed of calcium titanate (CaTiO_3). Its name is also applied to the class of compounds which have the same type of crystal structure as CaTiO_3 ($\text{XIIA}^{2+}\text{VIB}^{4+}\text{X}_{2-3}$), known as the perovskite structure. Many different cations can be embedded in this structure, allowing the development of diverse engineered materials. The mineral was discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist Lev Perovski (1792–1856). Perovskite's notable crystal structure was first described by Victor Goldschmidt in 1926 in his work on tolerance factors. The crystal structure was later published in 1945 from X-ray diffraction data on barium titanate by Helen Dick Megaw. Found in the Earth's mantle, perovskite's occurrence at Khibina Massif is restricted to the silica under-saturated ultramafic rocks and foidolites, due to the instability in a paragenesis with feldspar. Perovskite occurs as small anhedral to subhedral crystals filling interstices between the rock-forming silicates.

Perovskite is found in contact carbonate skarns at Magnet Cove, Arkansas, in altered blocks of limestone ejected from Mount Vesuvius, in chlorite and talc schist in the Urals and Switzerland, and as an accessory mineral in alkaline and mafic igneous rocks, nepheline syenite, melilitite, kimberlites and rare carbonatites. Perovskite is a common mineral in the Ca-Al-rich inclusions found in some chondritic meteorites. A rare-earth-bearing variety knopite ($(\text{Ca}, \text{Ce}, \text{Na})(\text{Ti}, \text{Fe})\text{O}_3$) is found in alkali intrusive rocks in the Kola Peninsula and near Alnö, Sweden. A niobium-bearing variety dysanalyte occurs in carbonatite near Schelingen, Kaiserstuhl, Germany.

Perovskites of the general formula ABX_3 may be regarded as derived from the ReO_3 structure as shown in Fig. 19.18. The BX_3 framework in the perovskite is similar to that in ReO_3 structure consisting of corner-shared BX_6 octahedra. The large A cation occupies the body center, 12-coordinate position. In an ideal cubic perovskite structure, Goldschmidt found that the perovskite structure is retained in ABX_3 compounds even when this relation is not exactly obeyed and defined a tolerance factor, t , as

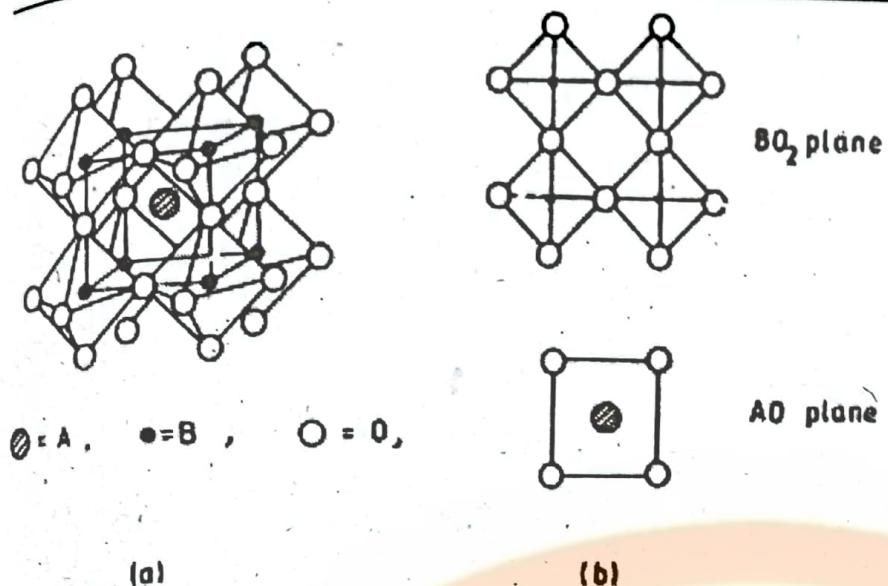


Figure 19.18. (a) The ABO_3 perovskite structure. Without the large A atom in the body center position, the structure becomes that of cubic ReO_3 ; (b) layer sequence in the perovskite structure parallel to (001).

Perovskites have a nearly cubic structure with the general formula ABO_3 . In this structure the A-site ion, in the center of the lattice, is usually an alkaline earth or rare-earth element. B-site ions, on the corners of the lattice, are 3d, 4d, and 5d transition metal elements. A large number of metallic elements are stable in the perovskite structure if the Goldschmidt tolerance factor 't' is in the range of 0.75–1.0

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)}$$

where R_A , R_B and R_O are the ionic radii of A and B site elements and oxygen, respectively. Perovskites have sub-metallic to metallic luster, colorless streak, and cube-like structure along with imperfect cleavage and brittle tenacity. Colors include black, brown, gray, orange to yellow. Perovskite crystals may appear to have the cubic crystal form, but are often pseudocubic and actually crystallize in the orthorhombic system, as is the case for $CaTiO_3$ (Strontium titanate, with the larger strontium cation in the A-site, is cubic). Perovskite crystals have been mistaken for galena; however, galena has a better metallic luster, greater density, perfect cleavage and true cubic symmetry. For the ideal perovskite structure, t is unity. The perovskite structure is, however, found for lower values of t ($\sim 0.75 < t \leq 1.0$), also. In such cases, the structure distorts to tetragonal, rhombohedral, or orthorhombic symmetry. This distortion arises from the smaller size of the A ion, which causes a tilting of the BX_6 octahedra in order to optimize A–X bonding. Perovskite oxides, ABO_3 , can be thought of as consisting of alternating BO_2 and AO layers stacked one over the other in the [001] direction. An alternative description of the ABO_3 structure in terms of close packing of A and O ions is one where close-packed AO_3 layers [Fig. 19.18a] are stacked one over the other with the B cations occupying octahedral holes surrounded by oxygen.

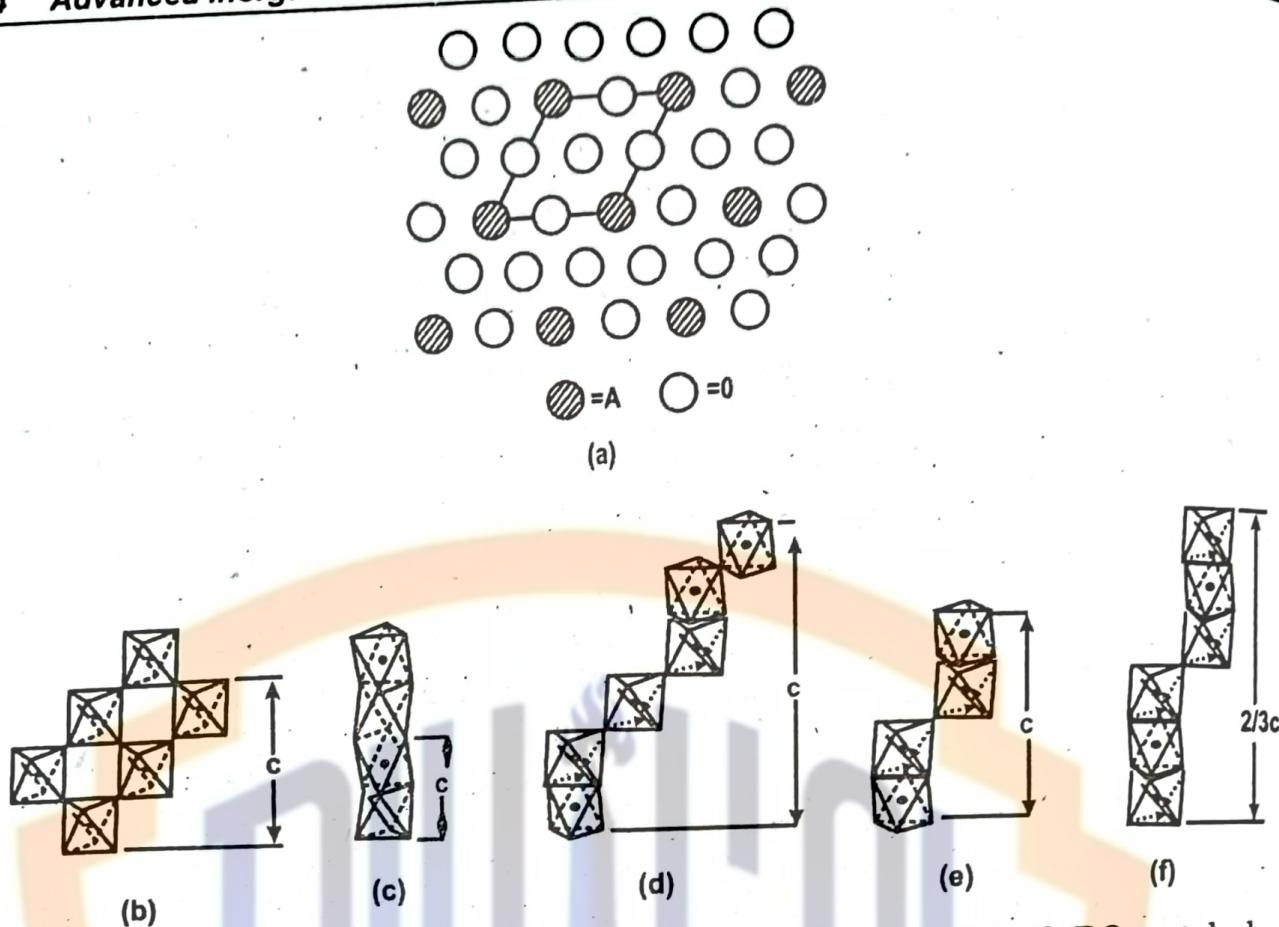


Figure 19.19 (a). (a) Close-packed AO_3 layer in perovskites. (b)–(f) BO_6 octahedra in different perovskite polytypes: (b) 3 C, (c) 2 H, (d) 6 H, (e) 4 H, and (f) 9 R.

Several ABO_3 oxides, where A is a large cation such as Ba and B is a small cation of the d-transition series, are known to exhibit polytypism. The stacking of an AO_3 layer in the structure may be cubic (c) or hexagonal (h) with respect to its two adjacent layers depending on whether it is in the middle of the ABA or ABC sequence. If the stacking is entirely cubic, the B-cation octahedra share only corners in three dimensions to form the perovskite (3 C) structure (Fig. 19.19). If the stacking is all hexagonal, the B-cation octahedra share opposite faces, forming chains along the c-axis as in BaNiO_3 (2 H). In between the two extremes, there can be several polytypic structures consisting of mixed cubic and hexagonal stacking of AO_3 layers; for example, the 6 H and 4 H polytypes have the stacking sequences cch cch and chch, respectively. Typical ABO_3 oxides showing polytypism are BaCrO_3 , BaMnO_3 , and BaRuO_3 .

Oxides of the general formula A_2BO_4 crystallize in the K_2NiF_4 structure, which is closely related to the perovskite structure. The tetragonal structure of K_2NiF_4 (Fig. 19.20) can be regarded as consisting of KNiF_3 perovskite slabs of one unit cell thick, which are stacked one over the other along the c-direction. The adjacent slabs are displaced relative to one another by 12 12 12, such that the c-axis of the tetragonal structure is roughly equal to three times the cell edge of the cubic perovskite. The structure is two-dimensional in the sense that only the equatorial anions of the NiF_6 octahedra are linked through corners. Tolerance factors for the K_2NiF_4 structure can be worked out just as for perovskites, and oxides of this structure often show orthorhombic distortion. Oxides of the K_2NiF_4 structure (for example, La_2CuO_4 , LaNiO_4) have been investigated extensively.

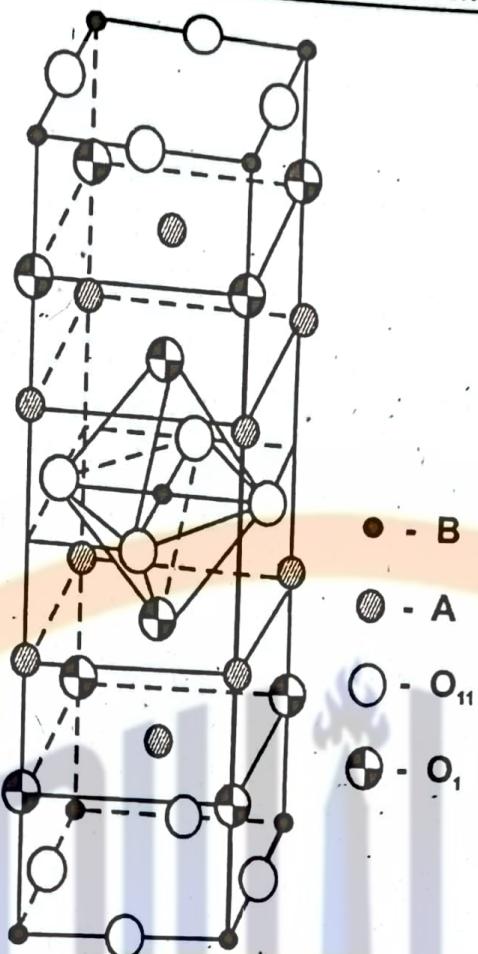


Figure 19.20. The K_2NiF_4 structure of oxides, A_2BO_4 .

The perovskite structure can tolerate vacancies at the A or X sites giving rise to nonstoichiometric compositions, $\text{A}_{(1-x)}\text{BX}_3$ and ABX_{3-x} . B-site vacancies are energetically not favored unless there are compensating factors such as B-B interaction. Typical examples of A-site vacancies are the tungsten bronzes, A_xWO_3 and $\text{Cu}_{0.5}\text{TaO}_3$; brownmillerite, $\text{CaFeO}_{2.5}$, is an example of an anion-deficient perovskite. Perovskite-type oxides also show anion excess nonstoichiometry as in the case of LaMnO_{3+x} , where the apparent anion excess probably arises from La vacancies. Examples of B-site vacancy hexagonal perovskites are $\text{Ba}_3\text{Re}_2\text{O}_9$ and $\text{Ba}_5\text{Nb}_4\text{O}_{15}$.

There are many other interesting oxide systems possessing perovskite units. There is a family of oxides, first described by Aurivillius, of the general formula $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$ containing $(\text{Bi}_2\text{O}_2)^{2+}$ layers and $(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$ perovskite layers. Typical members of this family are $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n=3$) and $\text{BaBi}_4\text{Ti}_4\text{O}_{15}$ ($n=4$). These oxides form disordered as well as ordered intergrowth structures. There are other intergrowth structures in oxides derived from the perovskite structure. Thus, the $\text{A}_n\text{B}_n\text{O}_{3n+2}$ family consists of slabs of $\text{A}_{n-1}\text{B}_n\text{O}_{3n+2}$ obtained by cutting the perovskite structure parallel to the (110) planes; a series of oxides with n between 4 and 4.5 is known in the Na-Ca-Nb-O system. The $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ family (for example, in Sr-Ti-O and La-Ni-O systems) is generated by cutting the perovskite structure into slabs along the (100) planes.

➤ Close Packed Ions

Ionic crystals can often be viewed as a close-packed arrangement of the larger ion, with the smaller ion placed in the "holes" of the structure.

Unit Cells

A unit cell of the crystal is an imaginary parallel-sided region from which the entire crystal can be built up.

The *space lattice* is the pattern formed by the points that represent these repeating structural units.

Close Packing

- 1- Cubic close packing
- 2- Hexagonal close packed

There are two types of holes created by a close-packed arrangement.

Octahedral Holes

The large spheres are in a cubic close-packed arrangement. The small spheres show the positions of octahedral holes in the unit cell. Each hole has a coordination number of 6. The size of the octahedral hole = $.414 r$, where r is the radius of the cubic close-packed atom or ion.

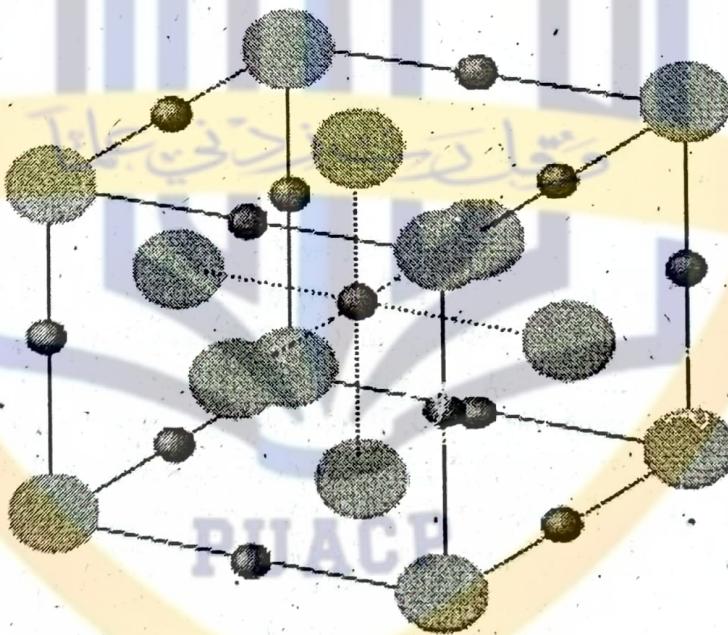


Figure 19.21. Octahedral Holes

Tetrahedral holes

Tetrahedral holes are formed by a planar triangle of atoms, with a 4th atom covering the indentation in the center. The resulting hole has a coordination number of 4.

The large spheres show atoms in a cubic close-packed arrangement. The small spheres behind each corner indicate the location of the tetrahedral holes. The size of the tetrahedral holes = $.225 r$, where r is the radius of the close-packed atom or ion.

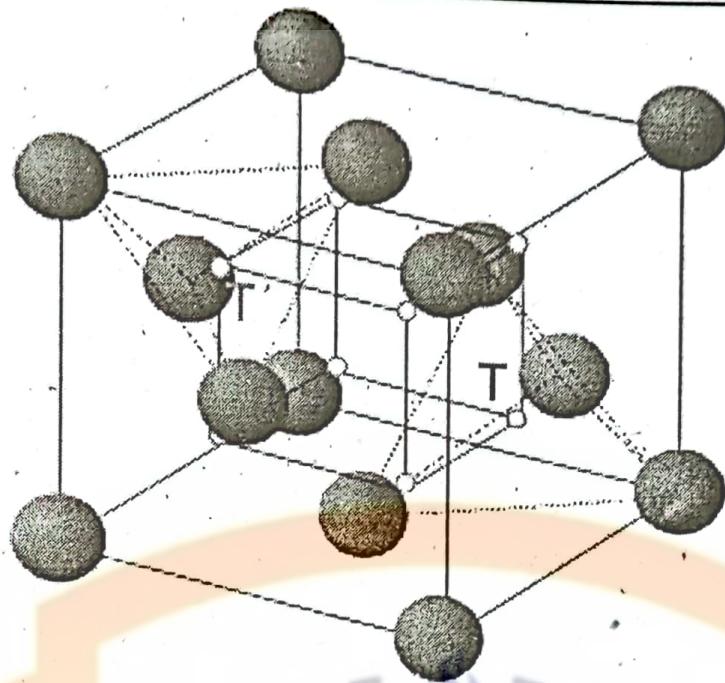


Figure 19.22. Tetrahedral holes

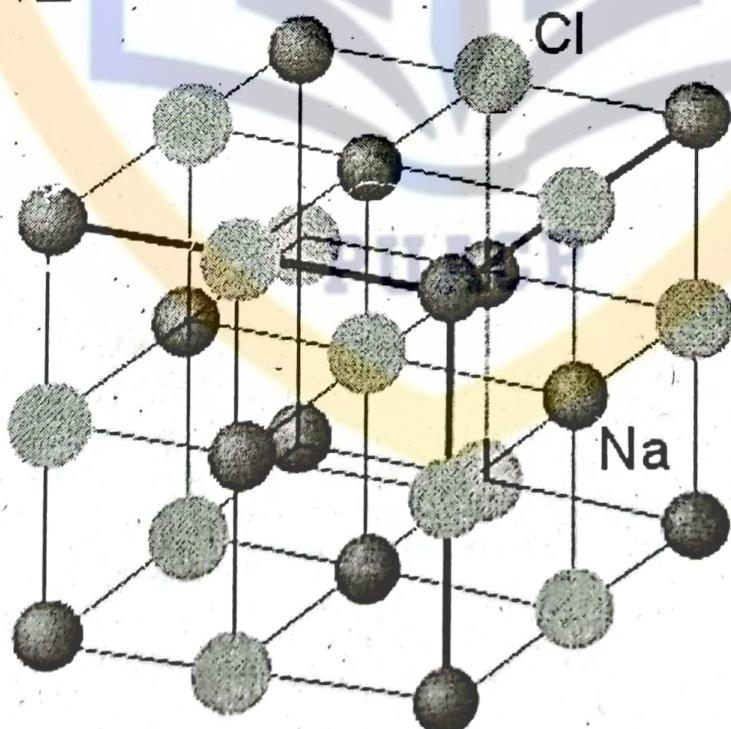
Ionic Compounds

Since anions are often larger than cations, ionic structures are often viewed as a close-packed array of anions with cations added, and sometimes distorting the close-packed arrangement.

Common Crystal Types

The Rock Salt (NaCl) structure

Can be viewed as a face-centered cubic array of the anions, with the cations in all of the octahedral holes, or

Figure 19.23. NaCl unit cell structure.

A face-centered cubic array of the cations with anions in all of the octahedral holes. The coordination number is 6 for both ions.

The CsCl structure

Chloride ions occupy the corners of a cube, with a cesium ion in the center (called a *cubic hole*) or vice versa. Both ions have a coordination number of 8, with the two ions fairly similar in size.

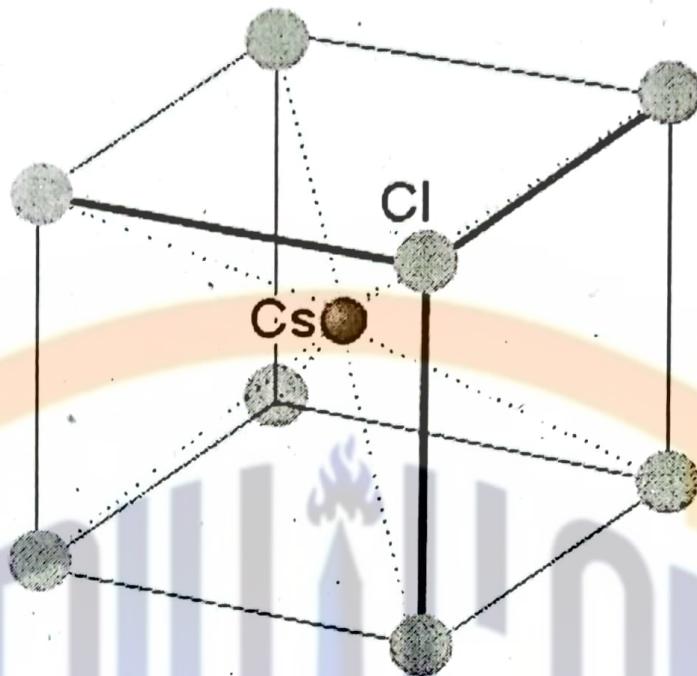


Figure 19.24. CsCl structure.

Most systems assign a radius to the oxide ion (often 1.26\AA), and the radius of the cation is determined relative to this assigned value.

1. Ionic radii increase as you go down a group.
2. Radii of ions of similar charge decrease across a period.
3. If an ion can be found in many environments, its radius increases with higher coordination number.
4. For cations, the greater the charge, the smaller the ion (assuming the same coordination No.).
5. For atoms near each other on the periodic table, cations are generally smaller than anions.

CN	r^+/r^-	Geometry	Examples
8	≥ 0.70	B.C.C	CsCl
6	0.4 - 0.7	Octahedral	NaCl
4	0.2 - 0.4	F.C.C	ZnS
3	0.10 - 0.20	Triangular	---

➤ Spinel

Spinel is the magnesium/aluminum member of the larger spinel group of minerals. It has the formula $MgAl_2O_4$ in the cubic crystal system. Its name comes from the Latin word spinella, which means spine in reference to its pointed crystals.

Spinel crystallizes in the isometric system; common crystal forms are octahedra, usually twinned. It has an imperfect octahedral cleavage and a conchoidal fracture. Its hardness is 8, its specific gravity is 3.5–4.1, and it is transparent to opaque with a vitreous to dull luster. It may be colorless, but is usually various shades of pink, rose, red, blue, green, yellow, brown, black, or (uncommon) violet. There is a unique natural white spinel, now lost, that surfaced briefly in what is now Sri Lanka. Some spinels are among the most famous gemstones; among them are the Black Prince's Ruby and the "Timur ruby" in the British Crown Jewels. The transparent red spinels were called spinel-rubies or balas rubies. In the past, before the arrival of modern science, spinels and rubies were equally known as rubies. After the 18th century the word ruby was only used for the red gem variety of the mineral corundum and the word spinel came to be used.

Spinel is found as a metamorphic mineral, and also as a primary mineral in rare mafic igneous rocks; in these igneous rocks, the magmas are relatively deficient in alkalis relative to aluminum, and aluminum oxide may form as the mineral corundum or may combine with magnesia to form spinel. This is why spinel and ruby are often found together. The spinel petrogenesis in mafic magmatic rocks is strongly debated, but certainly results from mafic magma interaction with more evolved magma or rock (e.g. gabbro, troctolite). Spinel, $(Mg,Fe)(Al,Cr)_2O_4$, is common in peridotite in the uppermost Earth's mantle. Spinel, $(Mg,Fe)Al_2O_4$, is a common mineral in the Ca-Al-rich inclusions (CAIs) in some chondritic meteorites.

Spinel has long been found in the gemstone-bearing gravel of Sri Lanka and in limestones of the Badakshan Province in modern-day Afghanistan and Tajikistan; and of Mogok in Myanmar. Over the last decades gem quality spinels are found in the marbles of Lục Yên District (Vietnam), Mahenge and Matombo (Tanzania), Tsavo (Kenya) and in the gravels of Tanzania and Madagascar.

Synthetic spinel, accidentally produced in the middle of the 18th century, has been described more recently in scientific publications in 2000 and 2004. By 2015, transparent spinel was being made in sheets and other shapes through sintering. Synthetic spinel, which looks like glass but has notably higher strength against pressure, can also have applications in military and commercial use.

The spinels are any of a class of minerals of general formulation AB_2X_4 which crystallise in the cubic (isometric) crystal system, with the X anions (typically chalcogens, like oxygen and sulfur) arranged in a cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice. Although the charges of A and B in the prototypical spinel structure are +2 and +3, respectively ($A^{2+}B^{3+}X^{2-}_4$), other combinations incorporating divalent, trivalent, or

tetravalent cations, including magnesium, zinc, iron, manganese, aluminum, chromium, titanium, and silicon, are also possible. The anion is normally oxygen; when other chalcogenides constitute the anion sublattice the structure is referred to as a thiospinel. A and B can also be the same metal with different valences, as is the case with magnetite, Fe_3O_4 (as $\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}^{2-}_4$), which is the most abundant member of the spinel group. Spinels are grouped in series by the B cation. Though spinels are often referred to as rubies, as in the Black Prince Ruby, the ruby is not a spinel.

Members of the spinel group include:

- 1) Aluminum spinels: Spinel: MgAl_2O_4 , after which this class of minerals is named, Gahnite: ZnAl_2O_4 , Hercynite: FeAl_2O_4 , Galaxite: MnAl_2O_4 , Pleonaste: $(\text{Mg},\text{Fe})\text{Al}_2\text{O}_4$
- 2) Iron spinels: Cuprospinel: CuFe_2O_4 , Franklinite: $(\text{Fe},\text{Mn},\text{Zn})(\text{Fe},\text{Mn})_2\text{O}_4$, Jacobsite: MnFe_2O_4 , Magnesioferrite: MgFe_2O_4 , Magnetite: FeFe_2O_4 , where one Fe is +2 and two Fe's are +3, respectively, Trevorite: NiFe_2O_4 , Ulvöspinel: TiFe_2O_4 , Zinc ferrite: $(\text{Zn},\text{Fe})\text{Fe}_2\text{O}_4$
- 3) Chromium spinels: Chromite: FeCr_2O_4 , Magnesiochromite: MgCr_2O_4 , Zincochromite: ZnCr_2O_4
- 4) Cobalt spinels: Manganesecobaltite: $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$
- 5) Vanadium spinels: Coulsonite: FeV_2O_4 , Magnesiocoulsonite: MgV_2O_4

Others with the spinel structure:

- 6) Ringwoodite: $(\text{Mg},\text{Fe})_2\text{SiO}_4$, an abundant olivine polymorph within the Earth's mantle from about 520 to 660 km depth, and a rare mineral in meteorites
- 7) Taaffeite: $\text{BeMgAl}_4\text{O}_8$ with an empirical formula as a spinel, but the chemical formula is four times as large.
- 8) Musgravite: $\text{Be}(\text{Mg},\text{Fe},\text{Zn})_2\text{Al}_6\text{O}_{12}$ a type of "multi-spinel".

There are many more compounds with a spinel structure, e.g. the thiospinels and selenospinels, that can be synthesized in the lab or in some cases occur as minerals. The heterogeneity of spinel group members varies based on composition with ferrous and magnesium-based members varying greatly as in solid solution, which requires similarly sized cations. However, ferric and aluminum based spinels are almost entirely homogeneous due to their large size difference.

Ferrites—whose etymology is from the Latin word ferrum meaning iron—are a large class of oxides containing Fe^{3+} and at least another metal cation that have been investigated and applied as powder, films or ceramic bodies for the last 50 years. They are classified according to their crystal structure and the way the oxygen anions are arranged around the metal cations, as spinel, garnet, magnetoplumbite and orthoferrite. While spinel and garnet ferrites both crystallize within a cubic structure, magnetoplumbites and orthoferrites crystallize within a hexagonal and orthorhombic structure, respectively.

Spinel ferrites are compounds with a general chemical formula MFe_2O_4 where M refers to a divalent metal cation, and that crystallize in a crystallographic

structure isomorphic with that of the naturally occurring mineral spinel $MgAl_2O_4$ (AB_2O_4 as general composition). They crystallize in a cubic symmetry structure containing eight formula units $A[B]_2O_4$, with a rigid sublattice of 32 closely packed oxygen anions giving rise to 64 tetrahedral (A)-type and 32 octahedral [B]-type interstitial sites partially occupied by 24 M^{2+} and Fe^{3+} metal cations (Fig. 19.25). Depending on the synthetic conditions, tetragonal unit cells can be obtained as well. In the spinel ferrites, the electrical neutrality is maintained by M^{2+} and Fe^{3+} cations occupying both tetrahedral and octahedral interstitial sites. The interstitial fourfold and sixfold sites have r_t and r_o radii in the $0.055 \text{ nm} < r_t < 0.067 \text{ nm}$ and $0.070 \text{ nm} < r_o < 0.075 \text{ nm}$ range, so that they can be occupied by many transition metal cations with d^0 to d^{10} electronic configurations. The octahedral vs. tetrahedral site occupation—and therefore the spinel ferrite structure—is reported to be driven by the electrostatic contribution to the lattice energy, the cation radii, the cation charge and the crystal field effect.

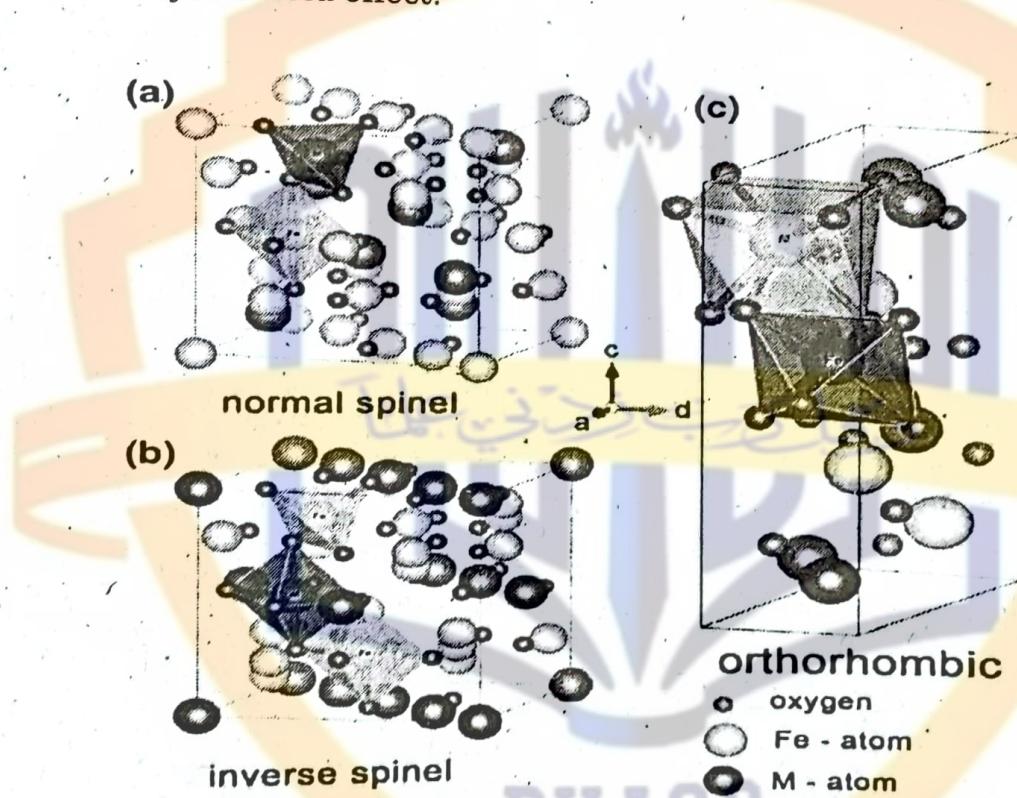


Figure 19.25. Crystallographic structure of AB_2O_4 spinel ferrites schematizing the different crystallographic sites: a normal spinel, b inverse spinel and c orthorhombic.

According to the M^{2+} and Fe^{3+} metal cation balance between both tetrahedral and octahedral sites, the spinel ferrites are categorized as follows:

- Normal spinels:** $(M^{2+})^{T_d}[Fe^{3+}]^{O_h}O_4$, in which the smaller divalent M^{2+} cations occupy only the tetrahedral A-sites and the trivalent Fe^{3+} cations occupy the octahedral B-sites, e.g. $ZnFe_2O_4$ or $CdFe_2O_4$.

- Inverse spinels:** $(Fe^{3+})^{T_d}[M^{2+}Fe^{3+}]^{O_h}O_4$ in which the divalent M^{2+} cations are located in the octahedral B-sites, while the trivalent Fe^{3+} cations are equally distributed between both tetrahedral A-sites and octahedral B-sites, e.g. $MgFe_2O_4$, $CoFe_2O_4$, $CuFe_2O_4$, $NiFe_2O_4$, $NiCoFe_2O_4$, $CuMnFe_2O_4$ or $MgCuFe_2O_4$.

- Mixed spinels** $(M^{2+}xFe^{3+}y)^{T_d}[M^{2+}_{1-x}Fe^{3+}_{2-y}]^{O_h}O_4$, in which both the divalent M^{2+} and trivalent Fe^{3+} cations are distributed between both tetrahedral A-sites and

octahedral B-sites, e.g. $\text{NiZnFe}_2\text{O}_4$, ZnFe_2O_4 , $\text{ZnMnFe}_2\text{O}_4$. Some spinel ferrites, such as: MgFe_2O_4 , CaFe_2O_4 and BaFe_2O_4 , are also reported to crystallize as orthorhombic phases (Fig. 19.24c).

Garnets are ferrites with a general chemical formula $\text{M}_3\text{Fe}_5\text{O}_{12}$, where M is a rare-earth cation. They crystallize in the structure of the $\text{X}_3\text{Y}_2(\text{SiO}_4)_3$ silicate mineral garnet, in which the X and Y sites are usually occupied by divalent (Ca^{2+} , Mg^{2+} , Fe^{2+}) and trivalent (Al^{3+} , Fe^{3+} , Cr^{3+}) cations, respectively, while the $(\text{SiO}_4)^{4-}$ units provide a tetrahedral framework. They crystallize in the cubic system, within a relatively complex structure based on a unit cell composed of eight formula units. Three kinds of cation sites coexist within this structure, and the cation distribution is usually expressed as $\{\text{M}_3\}\{\text{Fe}_3\}\{\text{Fe}_2\}\text{O}_{12}$. The M rare-earth cations occupy the largest dodecahedral (eightfold) sites, while the Fe^{3+} cations distribute among both tetrahedral (fourfold) and octahedral (sixfold) sites. By contrast to the spinel structure, the oxygen sublattice is better described as a polyhedral arrangement rather than as a close-packed one.

Crystal structure of spinel

The space group for a spinel group mineral is same as for diamond, but in some cases (like: spinel itself MgAl_2O_4) it is actually the tetrahedral. Normal spinel structures are usually cubic close-packed oxides with eight tetrahedral and four octahedral sites per formula unit. The tetrahedral spaces are smaller than the octahedral spaces. B ions occupy half the octahedral holes, while A ions occupy one-eighth of the tetrahedral holes. The mineral spinel MgAl_2O_4 has a normal spinel structure. Every ion is on at least three mirror planes and at least one three-fold rotation axis. The structure has tetrahedral symmetry around each A ion, and the A ions are arranged just like the carbon atoms in diamond.

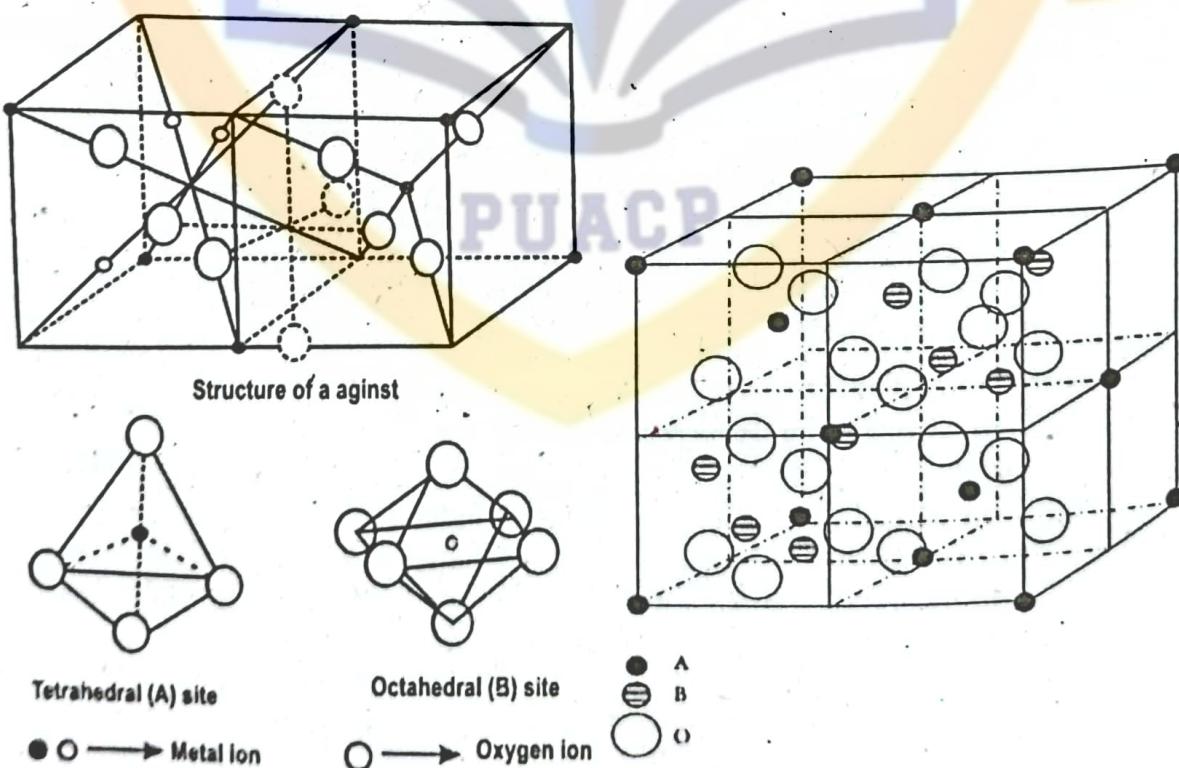


Figure 19.26. The spinel structure.

Inverse spinel structures have a different cation distribution in that all of the A cations and half of the B cations occupy octahedral sites, while the other half of the B cations occupy tetrahedral sites. An example of an inverse spinel is Fe_3O_4 , if the Fe^{2+} (A^{2+}) ions are d^6 high-spin and the Fe^{3+} (B^{3+}) ions are d^5 high-spin. In addition, intermediate cases exist where the cation distribution can be described as $(\text{A}_{1-x}\text{B}_x)[\text{A}_{\frac{x}{2}}\text{B}_{1-\frac{x}{2}}]_2\text{O}_4$, where parentheses () and brackets [] are used to denote tetrahedral and octahedral sites, respectively. The so-called inversion degree, x , adopts values between 0 (normal) and 1 (inverse), and is equal to $\frac{1}{3}$ for a completely random cation distribution. The cation distribution in spinel structures are related to the crystal field stabilization energies (CFSE) of the constituent transition metals. Some ions may have a distinct preference for the octahedral site depending on the d -electron count. If the A^{2+} ions have a strong preference for the octahedral site, they will displace half of the B^{3+} ions from the octahedral sites to tetrahedral sites. Similarly, if the B^{3+} ions have a low or zero *octahedral site stabilization energy* (OSSE), then they will occupy tetrahedral sites, leaving octahedral sites for the A^{2+} ions.

Common uses in industry and technology

Spinel commonly form in high temperature processes. Either native oxide scales of metals, or intentional deposition of spinel coatings can be used to protect base metals from oxidation or corrosion. The presence of spinels may hereby serve as thin (few micrometer thick) functional layers, that prevent the diffusion of oxygen (or other atmospheric) ions or specific metal ions such as chromium, which otherwise exhibits a fast diffusion process at high temperatures.

Ferrites are a large class of oxides containing Fe^{3+} and at least another metal cation that have been investigated for and applied to a wide variety of fields ranging from mature technologies like circuitry, permanent magnets, magnetic recording and microwave devices to the most recent developments in areas like bioimaging, gas sensing and photocatalysis. In the last respect, although ferrites have been less studied than other types of semiconductors, they present interesting properties such as visible light absorption, tuneable optoelectronic properties and high chemical and photochemical stability.

The versatility of their chemical composition and of their crystallographic structure opened a playground for developing new catalysts with enhanced efficiency. This article reviews the recent development of the application of ferrites to photoassisted processes for environmental remediation and for the synthesis of solar fuels. Applications in the photocatalytic degradation of pollutants in water and air, photo-Fenton, and solar fuels production, via photocatalytic and photoelectrochemical water splitting and CO_2 reduction, are reviewed paying special attention to the relationships between the physico-chemical characteristics of the ferrite materials and their photoactivated performance.

19.5 Environmental chemistry of volatile oxides

Volatile oxides are basically non metal oxides, like: Carbon, nitrogen or sulfur oxides. Their excessive emission from various industrial sources cause various problems to human being and ecosystem, like: acid rain and photochemical smog which can lead to stone cancer (corrosion of marble buildings, e.g: Taj Mahal), disturbing hatching process in fisheries, leaching of soluble nutrients (like: nitrates

and phosphates, which in turns leads to eutrophication or algal bloom in oceans that results in death of zooplanktons and decreased plant growth due to less availability of nutrients), skin diseases (like rashes, sclerosis), eye infections, throat and lungs damage in human beings and animals.

Nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and carbon monoxide are important ambient air pollutants. High-intensity, confined space exposure to NO_2 has caused catastrophic injury to humans, including death. Ambient NO_2 exposure may increase the risk of respiratory tract infections through the pollutant's interaction with the immune system. Sulfur dioxide (SO_2) contributes to respiratory symptoms in both healthy patients and those with underlying pulmonary disease. Controlled human exposure studies have demonstrated that experimental SO_2 exposure causes changes in airway physiology, including increased airways resistance. Both acute and chronic exposure to carbon monoxide are associated with increased risk for adverse cardiopulmonary events, including death. However, studies have not demonstrated a clear dose-dependent health risk response to increasing amounts of these pollutants except at high concentrations. In addition, a number of studies examining the effects of ambient level exposure to NO_2 , SO_2 , and CO have failed to find associations with adverse health outcomes.

These oxides chemistry is summarized below:

(i) Carbon Monoxide (CO)

Carbon monoxide (CO) is a colorless, odorless gas emitted from combustion processes. In urban areas, the majority of CO emissions to ambient air come from mobile sources. This gas consists during incomplete combustion of fuels. When we let a car engine run in a closed room, carbon monoxide concentrations in the air will rise extensively. Carbon monoxide contributes to the greenhouse effect, smog and acidification.

Health - Effects of CO air pollution.

CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. The gas can bind to haemoglobin in blood, preventing oxygen transport through the body. This results in oxygen depletion of the heart, brains and blood vessels, eventually causing death. At extremely high levels, CO can cause death.

Exposure to CO can reduce the oxygen-carrying capacity of the blood. For the people with heart diseases, short-term CO exposure further affects their body's already compromised ability to respond to the increased oxygen demands of exercise or exertion.

(ii) Carbon dioxide

It occurs naturally in the atmosphere. It is an essential ingredient in photosynthesis, the process by which plants make food and energy. Levels of atmospheric carbon dioxide have increased since the Industrial Revolution.

Sources

Combustible fossil fuels such as coal, power plant gas, oil, vehicles and big industry are the largest source of carbon dioxide. The production is from various items such as iron, steel, cement, natural gas, solid waste combustion, lime, ammonia, limestone, cropland, soda ash, aluminum, petrochemical, titanium and phosphoric acid. Carbon dioxide accounts for nearly 85 percent of all emissions and is produced when natural

gas, petroleum and coal are used. The major areas where these fuels are used include electricity generation, transportation, industry and in residential and commercial buildings.

The primary causes are deforestation and the burning of fossil fuels such as coal. As carbon dioxide levels have risen, so have its effects on air pollution. Carbon dioxide accounts for less than 1 percent of the atmospheric gases. However, a delicate balance exists between carbon dioxide and other gases. The concern over carbon dioxide is the significant change over a relatively short period of time.

(a) Greenhouse Effect

Carbon dioxide contributes to air pollution in its role in the greenhouse effect. Carbon dioxide traps radiation at ground level, creating ground-level ozone. This atmospheric layer prevents the earth from cooling at night. One result is a warming of ocean waters. Oceans absorb carbon dioxide from the atmosphere. However, higher water temperatures compromise the oceans' ability to absorb carbon dioxide. Over time, the effects of carbon dioxide are compounded.

Carbon dioxide is a naturally occurring greenhouse gas. Others include water vapor, methane and nitrous oxide. These gases help keep the Earth warm by absorbing the sun's energy and by redirecting energy back to the Earth's surface. An increase in the amount of carbon dioxide creates an overabundance of greenhouse gases that trap additional heat. This trapped heat leads to melting ice caps and rising ocean levels, which cause flooding.

Plants remove carbon dioxide from the atmosphere in a process called carbon sequestration. The carbon dioxide is stored in biomass then released by the plant. In most cases, the amount released is less than the amount consumed by the plant. Farms, grasslands and forests are considered sources or sinks of carbon dioxide, depending on the practices on these lands. For example, cows produce methane, but grass on the farm sequesters the gas.

(b) Climate Change

Another environmental effect of carbon dioxide on air pollution is climate change. The earth's surface temperature has risen over the last 100 years, according to studies done by the National Oceanic and Atmospheric Administration (NOAA). Scientists believe carbon dioxide pollution is the primary culprit. The effects are highly complex. Evidence shows, however, that ocean water levels have increased, resulting in a loss of shoreline and coastal wetlands.

(c) Acid Rain

Carbon dioxide is a contributor to the environmental effect known as acid rain. Emissions released from fossil fuel-burning energy plants combine with moisture in the air. The result is precipitation with a high acid content. Documented evidence shows the physical damage to trees and other plant life. Water and soil pollution occur from the acidic precipitation. A complicating factor is the mobility of emissions. The effects of carbon dioxide can be seen and felt far from their sources, making their impacts on air pollution more serious.

Human Health Impacts

Pollution and carbon dioxide emissions can have a negative impact on human health. Carbon dioxide emissions impact human health by displacing oxygen in the atmosphere. Breathing becomes more difficult as carbon dioxide levels rise. In closed areas, high levels of carbon dioxide can lead to health complaints such as headaches. Carbon dioxide levels may indicate high levels of other harmful air pollutants such as volatile organic compounds which contribute to indoor air pollution.

(iii) Nitrogen dioxide (NO_2)

Nitrogen dioxide (NO_2) is one of a group of highly reactive gasses known as "oxides of nitrogen," or "nitrogen oxides (NO_x)."⁵ Other nitrogen oxides include nitrous acid and nitric acid. NO_2 is the component of greatest interest and the indicator for the larger group of nitrogen oxides. NO_2 forms quickly from emissions from cars, trucks and buses, power plants, and off-road equipment. In addition to contributing to the formation of ground-level ozone, and fine particle pollution, NO_2 is linked with a number of adverse effects on the respiratory system.

Health - Effects of NO_2 air pollution

Current scientific evidence links short-term NO_2 exposures, ranging from 30 minutes to 24 hours, with adverse respiratory effects including airway inflammation in healthy people and increased respiratory symptoms in people with asthma.

NO_x react with ammonia, moisture, and other compounds to form small particles. These small particles penetrate deeply into sensitive parts of the lungs and can cause or worsen respiratory disease, such as emphysema and bronchitis, and can aggravate existing heart disease, leading to increased hospital admissions and premature death.

(iv) Sulfur dioxide (SO_2)

Sulfur dioxide (SO_2) is one of a group of highly reactive gases known as "oxides of sulfur."⁵ The largest sources of SO_2 emissions are from fossil fuel combustion at power plants (73%) and other industrial facilities (20%). Smaller sources of SO_2 emissions include industrial processes such as extracting metal from ore, and the burning of high sulfur containing fuels by locomotives, large ships, and non-road equipment. SO_2 is linked with a number of adverse effects on the respiratory system.

SO_2 is the component of greatest concern and is used as the indicator for the larger group of gaseous sulfur oxides (SO_x). Other gaseous sulfur oxides (e.g. SO_3) are found in the atmosphere at concentrations much lower than SO_2 .

Health - Effects of SO_2 air pollution

Current scientific evidence links short-term exposures to SO_2 , ranging from 5 minutes to 24 hours, with an array of adverse respiratory effects, including bronchoconstriction and increased asthma symptoms.

How is acid rain formed?

Acid rain is formed high up in the atmosphere when SO_2 and NO_2 combine with water and sunlight. When this reaction forms acid it falls to the ground in the form of acid rain or snow.

What are the environmental effects of acid rain?

- harmful to plant life
- harmful to aquatic life
- causes damage to forests
- causes damage to vegetation
- corrodes statues and monuments

19.6 HIGH-TEMPERATURE SUPERCONDUCTIVITY

High-temperature superconductors (abbreviated high- T_c or HTS) are materials that have a superconducting transition temperature (T_c) above 30 K (-243.2°C). From 1960 to 1980, 30 K was thought to be the highest theoretically possible T_c . The first high- T_c superconductor was discovered in 1986 by IBM researchers Karl Müller and Johannes Bednorz, for which they were awarded the Nobel Prize in Physics in 1987.

Until Fe-based superconductors were discovered in 2008. The term high-temperature superconductor was used interchangeably with cuprate superconductor for compounds such as bismuth strontium calcium copper oxide (BSCCO) and yttrium barium copper oxide (YBCO).

"High-temperature" has two common definitions in the context of superconductivity:

1. Above the temperature of 30 K that had historically been taken as the upper limit allowed by BCS theory. This is also above the 1973 record of 23 K that had lasted until copper-oxide materials were discovered in 1986.
2. Having a transition temperature that is a larger fraction of the Fermi temperature than for conventional superconductors such as elemental mercury or lead. This definition encompasses a wider variety of unconventional superconductors and is used in the context of theoretical models.

The label high- T_c may be reserved by some authors for those with critical temperature greater than the boiling point of liquid nitrogen (77 K or -196°C). However, a number of materials - including the original discovery and recently discovered pnictide superconductors - had critical temperatures below 77K but are commonly referred to in publication as being in the high- T_c class.

Technological applications benefit from both the higher critical temperature being above the boiling point of liquid nitrogen and also the higher critical magnetic field (and critical current density) at which superconductivity is destroyed. In magnet applications the high critical magnetic field may be more valuable than the high T_c .

itself. Some cuprates have an upper critical field around 100 teslas. However, cuprate materials are brittle ceramics which are expensive to manufacture and not easily turned into wires or other useful shapes.

Two decades of intense experimental and theoretical research, with over 100,000 published papers on the subject, have discovered many common features in the properties of high-temperature superconductors, but as of 2009, there is no widely accepted theory to explain their properties. Cuprate superconductors (and other unconventional superconductors) differ in many important ways from conventional superconductors, such as elemental mercury or lead, which are adequately explained by the BCS theory. There also has been much debate as to high-temperature superconductivity coexisting with magnetic ordering in YBCO, iron-based superconductors, several ruthenocuprates and other exotic superconductors, and the search continues for other families of materials. HTS are Type-II superconductors, which allow magnetic fields to penetrate their interior in quantized units of flux, meaning that much higher magnetic fields are required to suppress superconductivity. The layered structure also gives a directional dependence to the magnetic field response.

History and progress

- April 1911 - Kamerlingh Onnes discovers superconductivity.
- April 1986 - The term high-temperature superconductor was first used to designate the new family of cuprate-perovskite ceramic materials discovered by Johannes Georg Bednorz and Karl Alexander Müller, for which they won the Nobel Prize in Physics. Their discovery of the first high-temperature superconductor, LaBaCuO, with a transition temperature of 30 K, generated great excitement.
- LSCO ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) discovered the same year.
- January 1987 - YBCO was discovered to have a T_c of 90 K.
- 1988 - BSCCO discovered with T_c up to 108 K, and TBCCO (T=thallium) discovered to have T_c of 127 K.
- As of 2009, the highest-temperature superconductor (at ambient pressure) is mercury barium calcium copper oxide ($\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$), at 135 K and is held by a cuprate-perovskite material, which possibly reaches 164 K under high pressure.
- Recently, iron-based superconductors with critical temperatures as high as 56 K have been discovered. These are often also referred to as high-temperature superconductors. After more than twenty years of intensive research the origin of high-temperature superconductivity is still not clear, but it seems that instead of electron-phonon attraction mechanisms, as in conventional superconductivity, one is dealing with genuine electronic mechanisms (e.g. by antiferromagnetic correlations), and instead of s-wave pairing, d-waves are substantial.

One goal of all this research is room-temperature superconductivity. However following numerous announcements of room-temperature superconductivity that were discredited on examination, most condensed matter physicists now treat with extreme skepticism any claims of this nature.

Examples

Examples of high-T_c cuprate superconductors include La_{1.85}Ba_{0.15}CuO₄, and YBCO (Yttrium-Barium-Copper-Oxide), which is famous as the first material to achieve superconductivity above the boiling point of liquid nitrogen.

(i) Cuprates

Simplified doping dependent phase diagram of cuprate superconductors for both electron (n) and hole (p) doping. The phases shown are the antiferromagnetic (AF) phase close to zero doping, the superconducting phase around optimal doping, and the pseudogap phase. Doping ranges possible for some common compounds are also shown. Cuprate superconductors are generally considered to be quasi-two-dimensional materials with their superconducting properties determined by electrons moving within weakly coupled copper-oxide (CuO₂) layers. Neighboring layers containing ions such as lanthanum, barium, strontium, or other atoms act to stabilize the structure and dope electrons or holes onto the copper-oxide layers. The undoped 'parent' or 'mother' compounds are Mott insulators with long-range antiferromagnetic order at low enough temperature. Single band models are generally considered to be sufficient to describe the electronic properties.

The cuprate superconductors adopt a perovskite structure. The copper-oxide planes are checkerboard lattices with squares of O²⁻ ions with a Cu²⁺ ion at the centre of each square. The unit cell is rotated by 45° from these squares. Chemical formulae of superconducting materials generally contain fractional numbers to describe the doping required for superconductivity. There are several families of cuprate superconductors and they can be categorized by the elements they contain and the number of adjacent copper-oxide layers in each superconducting block. For example, YBCO and BSCCO can alternatively be referred to as Y₁₂₃ and Bi₂₂₀₁/Bi₂₂₁₂/Bi₂₂₂₃ depending on the number of layers in each superconducting block (n). The superconducting transition temperature has been found to peak at an optimal doping value (p = 0.16) and an optimal number of layers in each superconducting block, typically n = 3.

(ii) Iron-based superconductor

Simplified doping dependent phase diagrams of iron-based superconductors for both Ln-1111 and Ba-122 materials. The phases shown are the antiferromagnetic/spin density wave (AF/SDW) phase close to zero doping and the superconducting phase around optimal doping. The Ln-1111 phase diagrams for La and Sm were determined using muon spin spectroscopy, the phase diagram for Ce was determined using neutron diffraction. The Ba-122 phase diagram is based on.

Iron-based superconductors contain layers of iron and a pnictogen—such as arsenic or phosphorus—or a chalcogen. This is currently the family with the second highest critical temperature, behind the cuprates. Interest in their superconducting properties began in 2006 with the discovery of superconductivity in LaFePO at 4 K and gained much greater attention in 2008 after the analogous material LaFeAs(O,F) was found to superconduct at up to 43 K under pressure.

Since the original discoveries several families of iron-based superconductors have emerged. Most undoped iron-based superconductors show a tetragonal-orthorhombic structural phase transition followed at lower temperature by magnetic

ordering, similar to the cuprate superconductors. However, they are poor metals rather than Mott insulators and have five bands at the Fermi surface rather than one. The phase diagram emerging as the iron-arsenide layers are doped is remarkably similar, with the superconducting phase close to or overlapping the magnetic phase. Strong evidence that the T_c value varies with the As-Fe-As bond angles has already emerged and shows that the optimal T_c value is obtained with undistorted FeAs_4 tetrahedral. The symmetry of the pairing wave function is still widely debated, but an extended s-wave scenario is currently favored.

Other materials sometimes referred to as high-temperature superconductors:

- (iii) **Magnesium diboride** is occasionally referred to as a high-temperature superconductor because its T_c value of 39 K is above that historically expected for BCS superconductors. However, it is more generally regarded as the highest T_c conventional superconductor, the increased T_c resulting from two separate bands being present at the Fermi energy.
- (iv) **Fulleride superconductors** where alkali-metal atoms are intercalated into C_{60} molecules show superconductivity at temperatures of up to 38 K for Cs_3C_{60} .
- (v) Some **organic superconductors and heavy fermion compounds** are considered to be high-temperature superconductors because of their high T_c values relative to their Fermi energy, despite the T_c values being lower than for many conventional superconductors. This description may relate better to common aspects of the superconducting mechanism than the superconducting properties.
- (vi) Theoretical work by Neil Ashcroft in 1968 predicted that **solid metallic hydrogen** at extremely high pressure should become superconducting at approximately room-temperature because of its extremely high speed of sound and expected strong coupling between the conduction electrons and the lattice vibrations. This prediction is yet to be experimentally verified.

All known high- T_c superconductors are Type-II superconductors. In contrast to Type-I superconductors, which expel all magnetic fields due to the Meissner effect, Type-II superconductors allow magnetic fields to penetrate their interior in quantized units of flux, creating "holes" or "tubes" of normal metallic regions in the superconducting bulk. Consequently, high- T_c superconductors can sustain much higher magnetic fields.

QUESTIONS

- Q1. How many tetrahedral and octahedral voids would you expect from the cubic close packing of N identical spheres? Also discuss the same if hcp, in place of fcc, is used.
- Q2. Draw and discuss the crystal structure of fluorite.
- Q3. How does the Na_2O structure differ from the crystal structure of CaF_2 ?
- Q4. What is rutile? Explain its structure.
- Q5. What is the periodic trend in chemical behavior of oxides?
- Q6. Define the term layered lattice. Draw and discuss tow examples in detail.
- Q7. Draw and discuss the crystal structure of β -Cristobalite.
- Q8. How does the crystal structure of ReO_3 differ from the perovskite? Explain with suitable diagram.
- Q9. Discuss the chemistry of Perovskites.
- Q10. What is calcite? Draw and discuss its crystal structure.
- Q11. What are Spinel? What are their types. Give some details about their crystalline structure and applications.
- Q12. What are the toxic effects of volatile oxides on ecosystem?
- Q13. What are High-temperature superconductors? Discuss their chemistry.
- Q14. Discuss the chemistry of closed packed ionic crystals.

MCQs

- 12) Boron is a
 a) metal
 b) non-metal
 c) metalloid
 d) gas
- 13) As we move across the period the basic character of oxides
 a) increases
 b) decreases
 c) remains same
 d) becomes zero
- 14) The oxide of aluminum is
 a) acidic
 b) neutral
 c) basic
 d) amphoteric
- 15) Select the correct statement about the oxoanions of sulfur:
 a) The SO_3^{2-} ion is a strong reducing agent; the sulfate ion is unreactive; the peroxydisulfate ion is a strong oxidizing agent.
 b) SO_3^{2-} is a strong oxidizing agent; SO_4^{2-} is a strong reducing agent; $\text{S}_2\text{O}_8^{2-}$ is unreactive.
 c) SO_3^{2-} is a strong reducing agent; SO_4^{2-} is a strong oxidizing agent; $\text{S}_2\text{O}_8^{2-}$ is unreactive.
 d) SO_3^{2-} is a strong reducing agent; SO_4^{2-} is unreactive; $\text{S}_2\text{O}_8^{2-}$ is strong oxidizing agent.

Answers :

- | | | |
|------|-------|-------|
| 1) c | 6) b | 11) a |
| 2) c | 7) c | 12) b |
| 3) a | 8) a | 13) c |
| 4) a | 9) a | 14) d |
| 5) c | 10) b | 15) a |

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