

CHAPTER 6

Crystal Structures:

❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI_2 , BiI_3 ; ReO_3 , Mn_2O_3 , Corundum, Perovskite, Ilmenite and Calcite.

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 1587. 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 two dimensions can be visualized in two arrangements as given below.

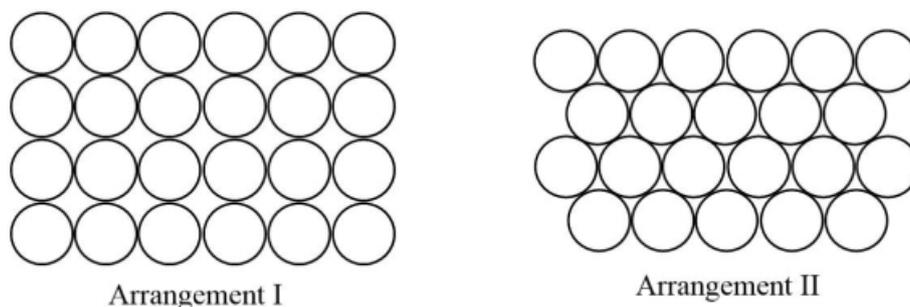


Figure 1. The close packing of identical spheres in two dimensions.

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.

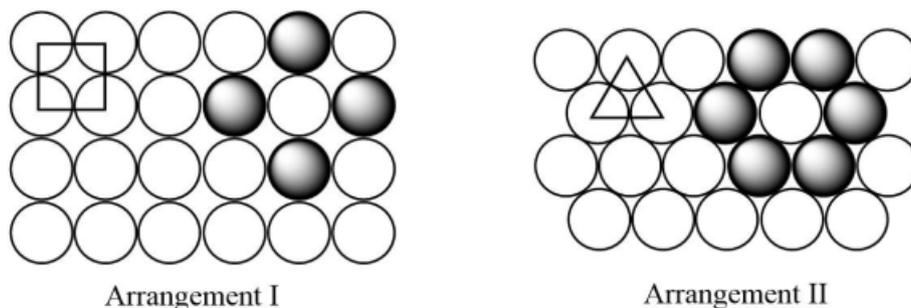


Figure 2. The coordination number and nearest sphere system in close packing of identical spheres in two dimensions.

The two-dimensional packing can successfully be extended to three-dimensional packing just by placing the other layers of packed identical spheres over it. This can be achieved in two ways as depicted below.

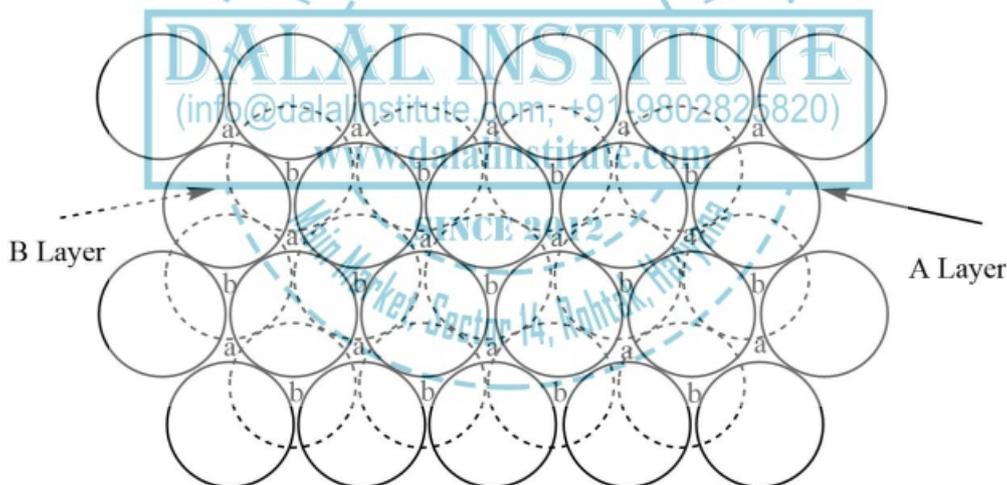


Figure 3. The extension of close packing of identical sphere systems in two dimensions to three dimensions.

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 $\sqrt{3}/2$ for the tetrahedral, and $\sqrt{2}$ for the octahedral when the sphere radius is unity.

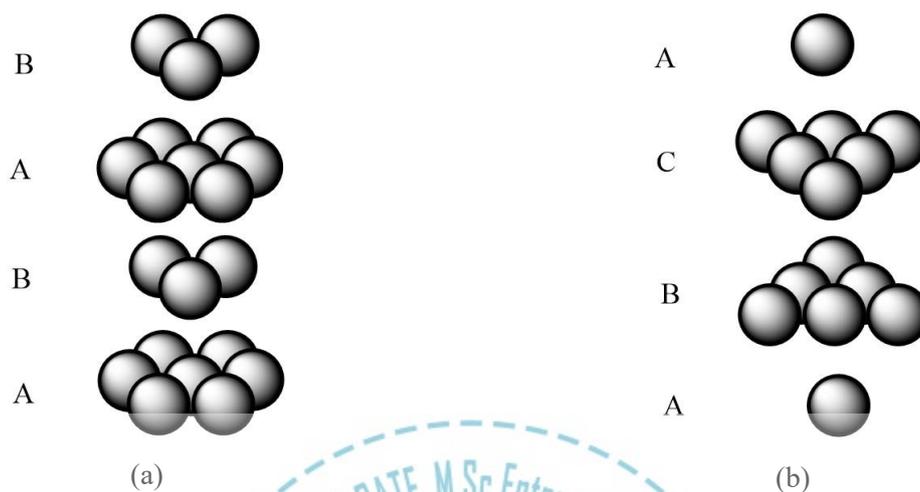


Figure 4. The illustration of the close-packing of equal spheres in both (a) hcp and (b) fcc lattices.

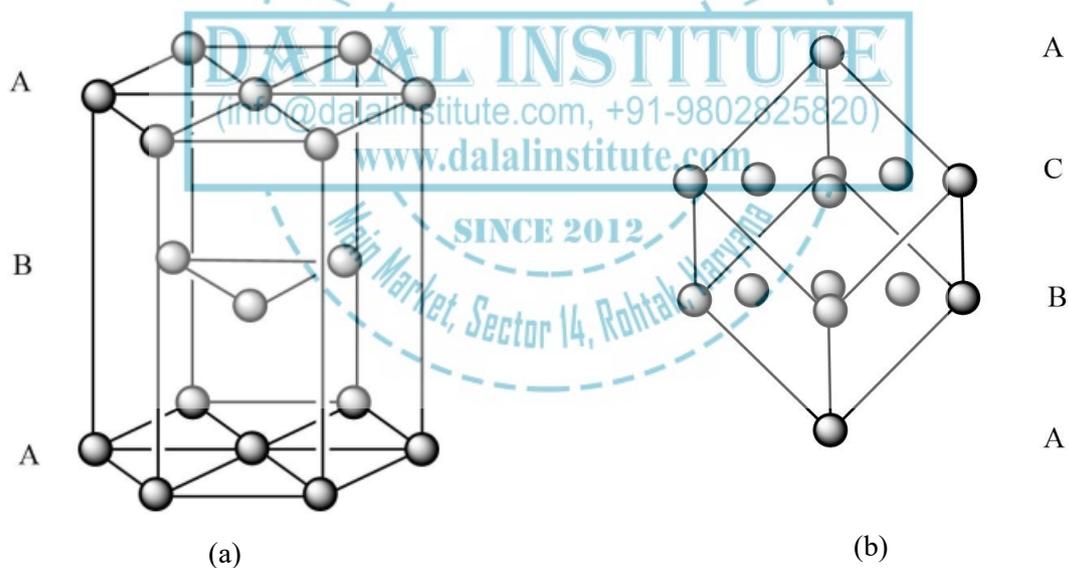


Figure 5. The ball and stick model of the close-packing of equal spheres in both (a) hcp and (b) fcc lattices.

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

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.

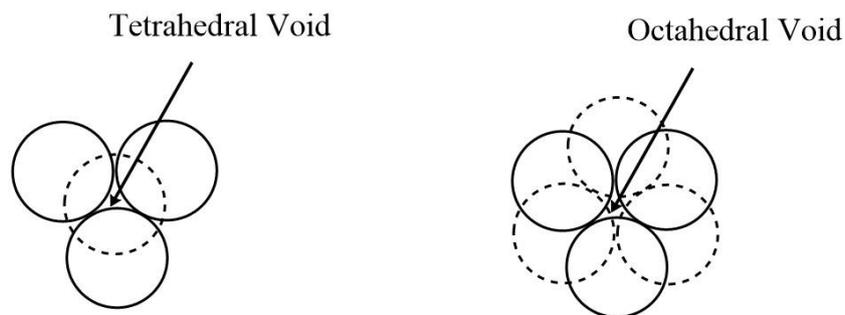


Figure 6. The formation of a tetrahedral and octahedral void in close packing of identical spheres in three dimensions.

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.

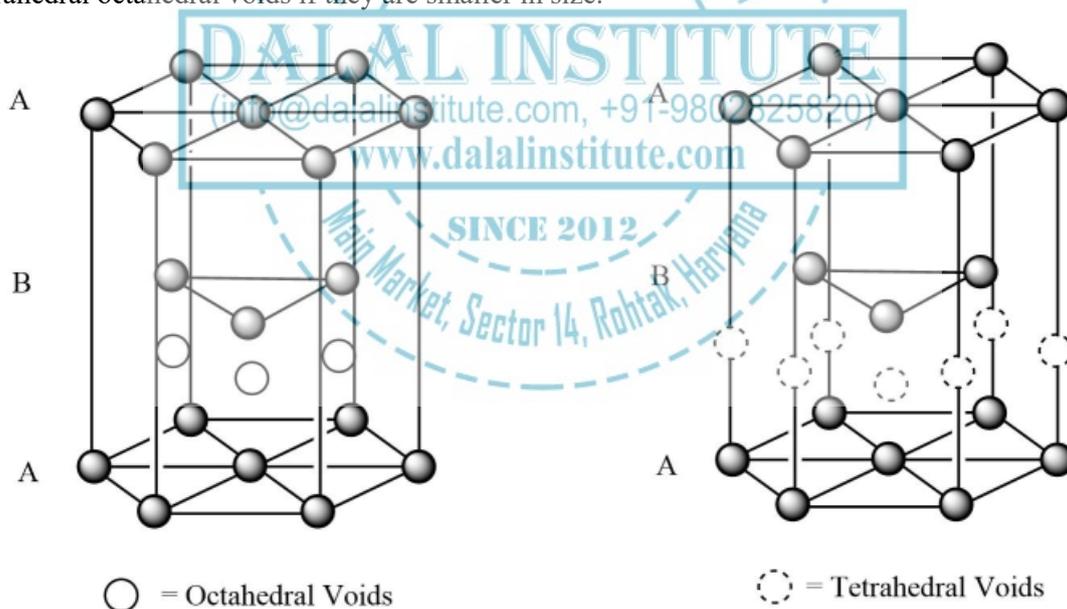


Figure 7. The location of octahedral and tetrahedral sites in hexagonal close packing or hcp lattices formed by the identical spheres.

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.

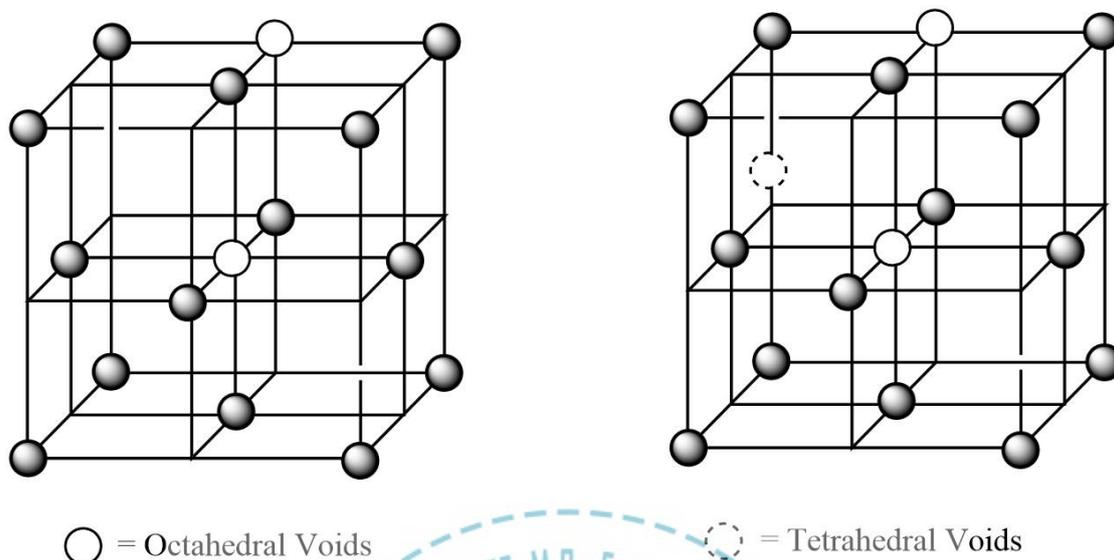


Figure 8. The location of octahedral and tetrahedral sites in cubic close packing or fcc lattices.

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.

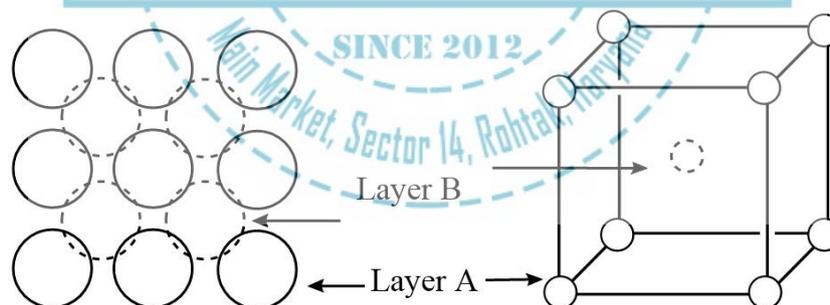


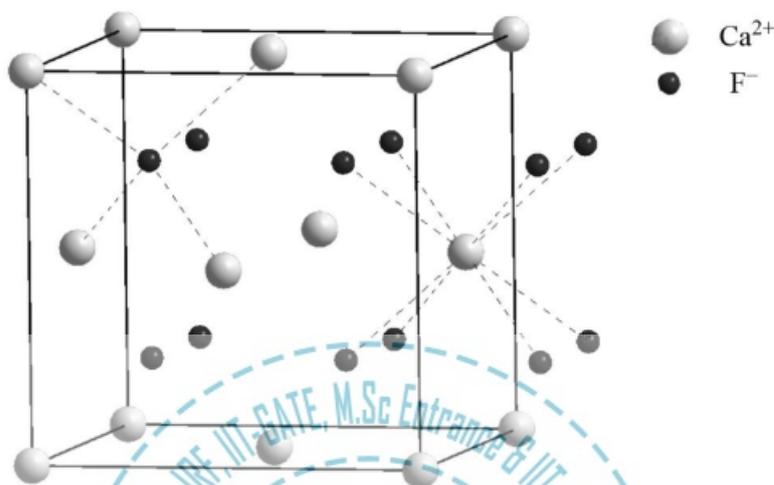
Figure 9. Body-centered close packing of equal spheres.

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.

➤ **Fluorite (CaF_2)**

Fluorite or fluorspar is the mineral form of calcium fluoride, CaF_2 . The unit cell of CaF_2 is shown below.



Structure of CaF_2
 Figure 10. The crystal structure of calcium fluoride or CaF_2 .
 (info@dalalinstitute.com, +91-9802825820)
 www.dalalinstitute.com

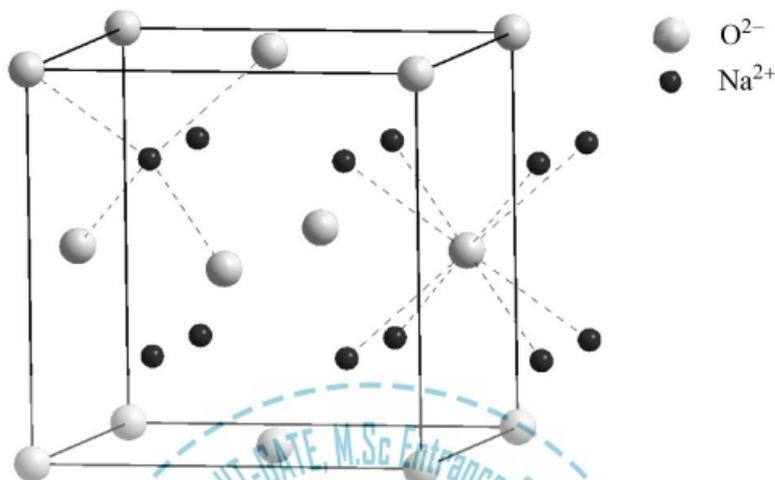
The main features of this crystal structure are as follows:

1. The Ca^{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 F^- 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 Ca^{2+} ion. Now, because all the tetrahedral sites are occupied by F^- anions, the stoichiometry of the compound becomes 1:2.
4. The coordination number of Ca^{2+} is eight while each F^- ion is surrounded by four calcium ions. The surrounding geometry of Ca^{2+} ion is tetrahedral and of F^- is cubical in nature. Therefore, the coordination number ratio of Ca^{2+} and F^- is 8:4.

The other common examples of this structural prototype of are CuF_2 , BaF_2 , PbF_2 , HgF_2 , SrF_2 . It is worthy to note that ideally packed samples are colorless but the mineral form of fluorite is usually deep in color, which is obviously due to the presence of F-centres. The high purity fluorite is a source of fluoride for the manufacturing of hydrofluoric acid, an intermediate source of most chemicals that contain fluorine. The transparent fluorites of high optical purity have low dispersion, and therefore, are used to make lenses with less chromatic aberration. This makes them valuable for the telescopes and microscopes devices.

➤ **Antifluorite (Na_2O)**

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



Structure of Na_2O

Figure 8. The crystal structure of calcium fluoride or Na_2O .

(info@dalalinstitute.com, +91-9802825820)

www.dalalinstitute.com

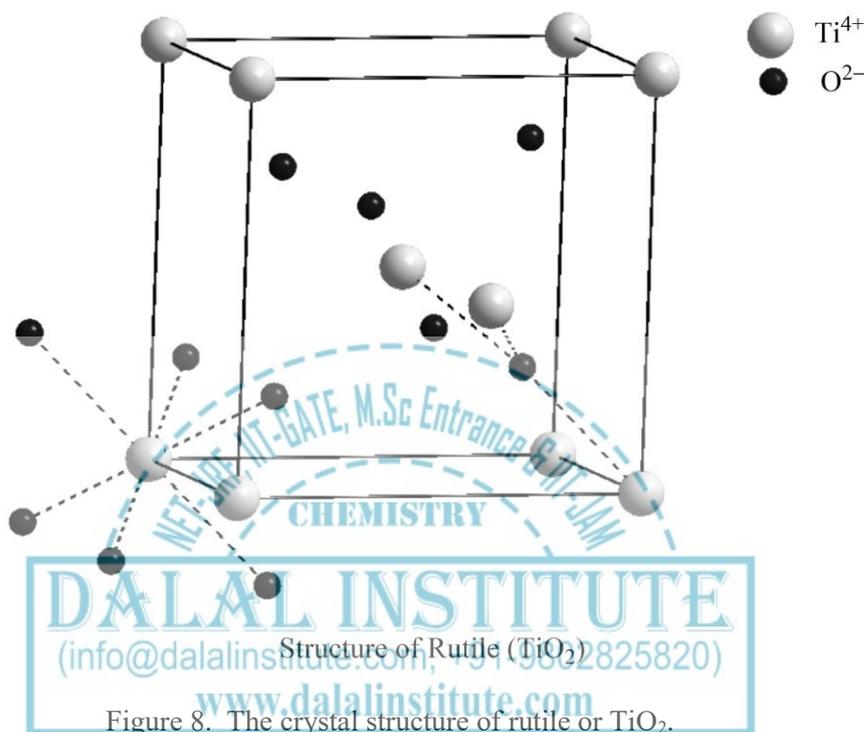
The main features of this crystal structure are as follows:

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 tetrahedral 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)**

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



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.

➤ **Antirutile (Ti_2N)**

Antirutile is the mineral form of titanium nitride, Ti_2N . The unit cell of Ti_2N lattice is shown below.

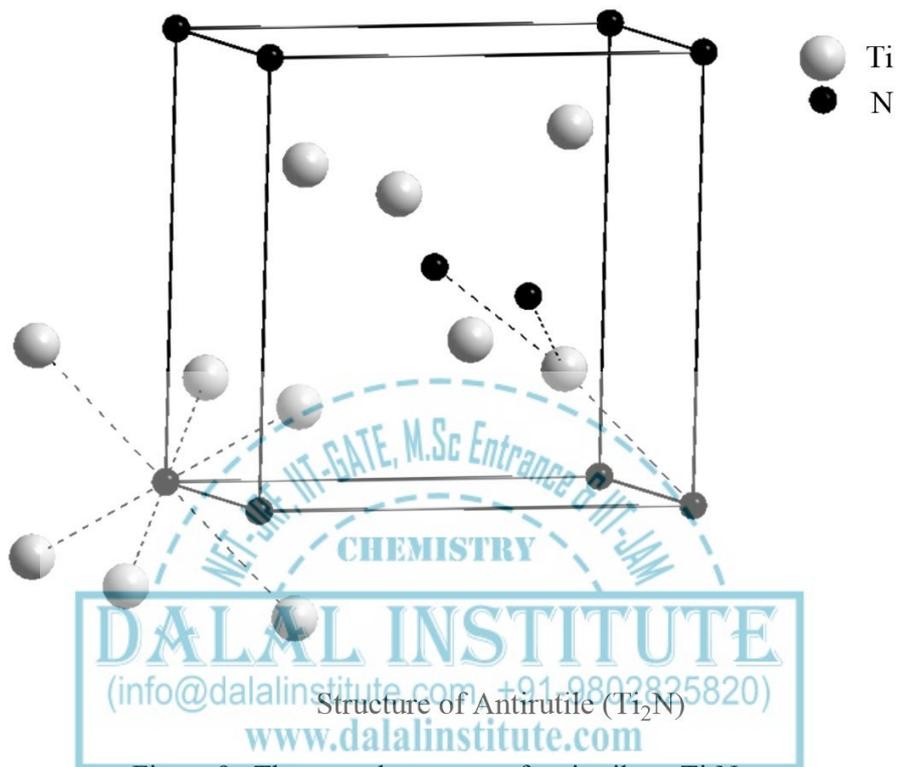


Figure 9. The crystal structure of antirutile or Ti_2N .

The main features of this crystal structure are as follows:

1. The nitride 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 nitride ions are surrounded by six titanium ions while each titanium ion is surrounded by three titanium ions. The coordinating geometry of titanium ion is trigonal and of nitride is octahedral in nature. Therefore, the coordination number ratio of Ti and N is 3:6.

It is worth noting that in this motif the positions of the anions and cations are reversed relative to their positions in TiO_2 (rutile), with titanium ions trigonally coordinated to three nitride ions and nitrides are cubically coordinated to six titanium ions. Therefore, the name antirutile is assigned due to the reversal of the positions of nitride and titanium ions. Seldom, the antirutile structure is encountered where the metal and non-metals have changed places. The number of formula units presents per unit cell is two, same as in case rutile structure.

➤ **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 metastably 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.

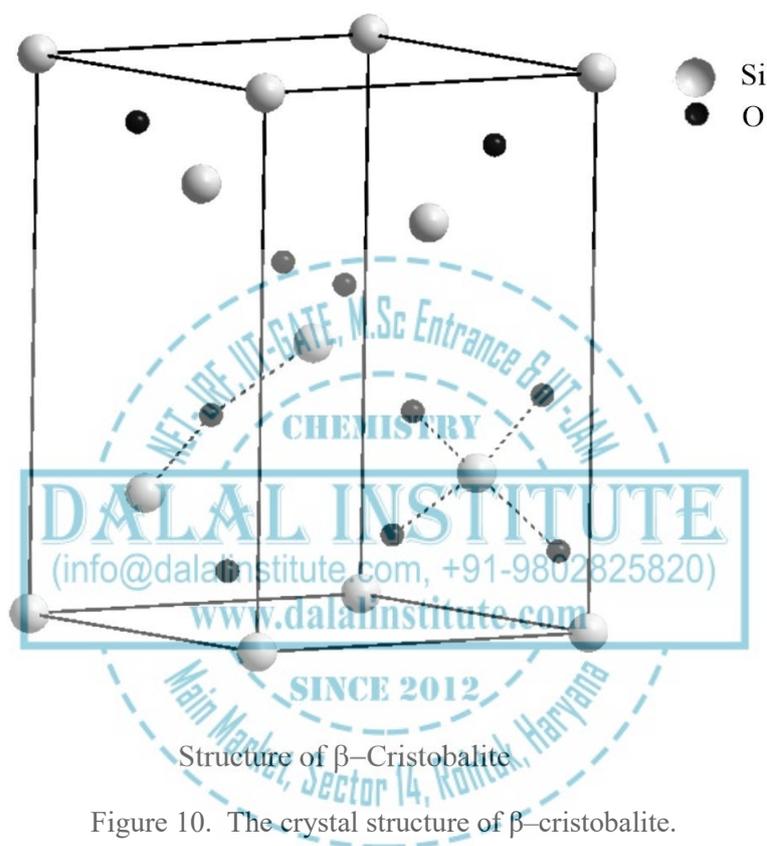


Figure 10. The crystal structure of β -cristobalite.

The main features of this crystal structure are as follows:

1. 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 octahedra 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.

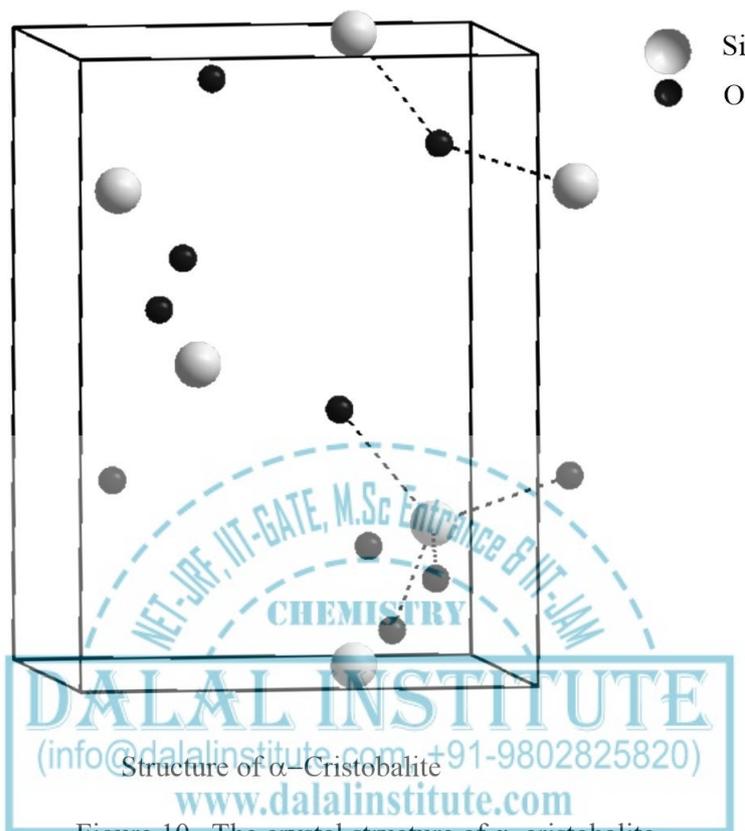


Figure 10. The crystal structure of α -cristobalite.

The main features of this crystal structure are as follows:

1. α -cristobalite crystallizes 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 4.

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 $\alpha - \beta$ 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 discontinuous 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.

➤ CdI_2

Cadmium iodide is a layered lattice of cadmium and iodine with formula CdI_2 . It is pretty much notable for its lattice profile, which is quite common for the MX_2 type compounds with strong polarization effects. The unit cell of CdI_2 is shown below.

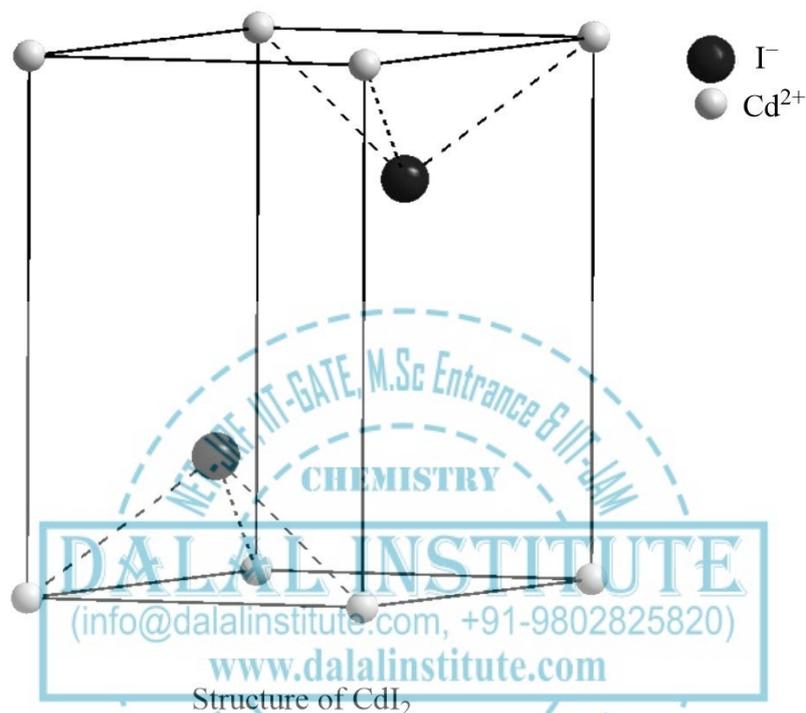
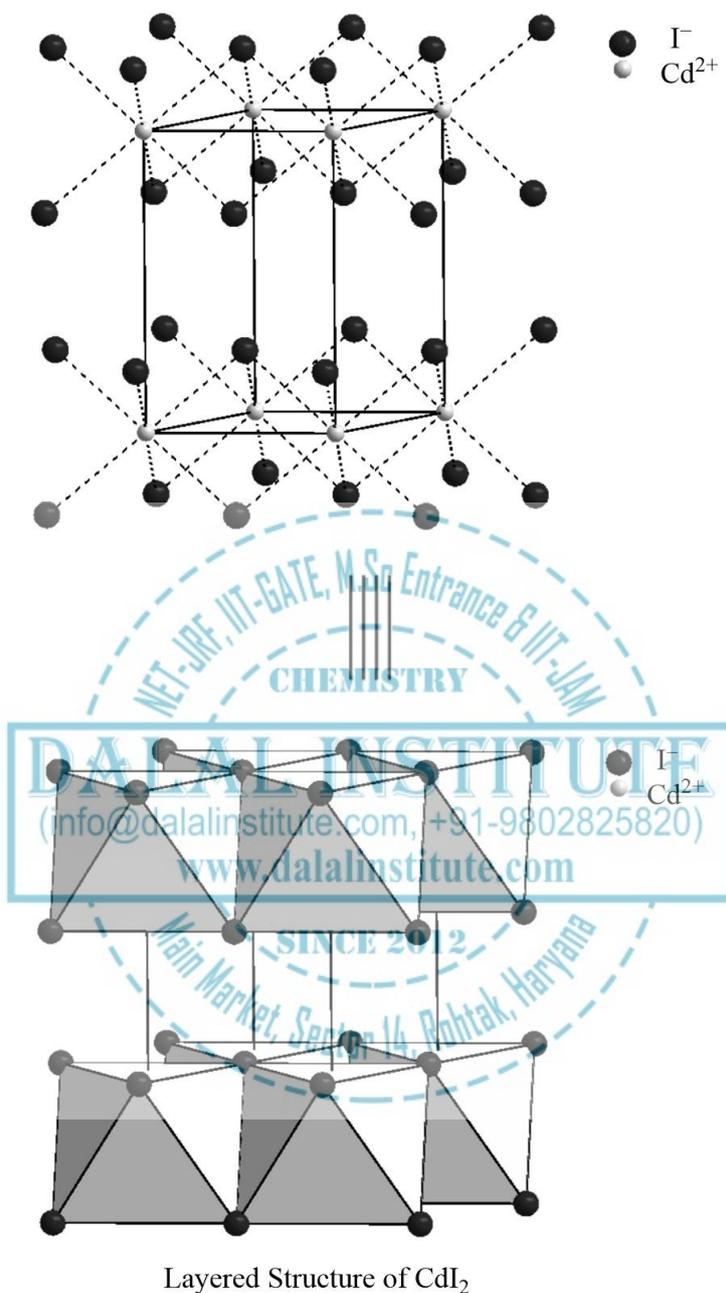


Figure 11. The unit cell of CdI_2 crystal system.

The main features of this crystal structure are as follows:

1. In cadmium iodide, the I^- anions form a hcp arrangement, while the Cd^{2+} cations fill all of the octahedral voids in the alternate layers.
2. Each Cd^{2+} ion is surrounded by six iodide ions while each I^- is coordinated by three cadmium cations. The coordinating geometry of cadmium ion is octahedral and of iodide ion is a trigonal pyramid in nature. Therefore, the coordination number ratio of Cd^{2+} and I^- is 6:3.
3. The resultant structure comprises of a layered lattice in which the Cd^{2+} ions are occupying all octahedral sites but in between the alternate layers of I^- . It can be visualized as if the cadmium ions layer is sandwiched between the two layers of iodide ions. Moreover, these sandwiched are piled over each other in such a way that the upward iodide ion layer of one sandwich is in contact with the downward iodide ion layer of the other sandwich. The same holds for the downward iodide-ion layer. This same basic structure is found in many other salts and minerals. This can be depicted as:

Figure 12. The crystal structure of CdI_2 .

4. Cadmium iodide is bonded mostly in ionic fashion but does have partial covalent character too.

The other examples of this type of structure are PbI_2 , MgI_2 , TiI_2 , VI_2 , TiCl_2 , VCl_2 , CoI_2 , FeI_2 , Mg(OH)_2 , Ni(OH)_2 and Ca(OH)_2 . Cadmium iodide is used in photography, electroplating, lithography and the synthesis of phosphors.

➤ **BiI_3**

Bismuth iodide, BiI_3 , is a layer lattice of bismuth and iodine. It is notable for its crystal structure, which is typical for MX_3 type compounds. The unit cell of BiI_3 is shown below.

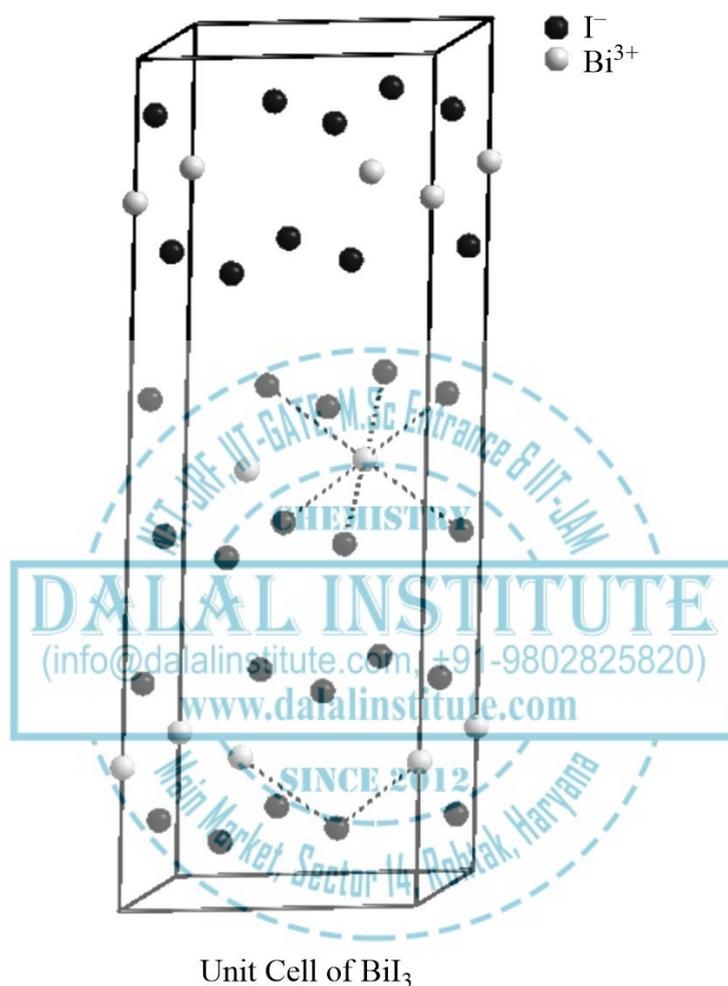


Figure 13. The unit cell of BiI_3 crystal system.

The main features of this crystal structure are as follows:

1. Bismuth iodide adopts a distinctive crystal structure, with I^- occupying a hcp lattice while bismuth centers occupy either none or two-thirds of the octahedral sites in the alternating layers. Hence, we can say that one-third of all octahedral sites are actually occupied.
2. Each Bi^{3+} ion is surrounded by six iodide ions while each I^- is coordinated by two bismuth cations. The coordinating geometry of bismuth ion is octahedral and of iodide ion is V-shaped in nature. Therefore, the coordination number ratio of Bi^{3+} and I^- is 6:2.

3. The resultant structure consists of a layered lattice. The Bi^{3+} ions are occupying one-third of all octahedral sites but in between the alternate layers of I^- . However, only two-third of all octahedral voids in every other layer are actually occupied. It can be visualized as if the bismuth ions layer is sandwiched between the two layers of iodide ions. Moreover, these sandwiched are piled over each other in such a way that the upward iodide ion layer of one sandwich is in contact with the downward iodide ion layer of the other sandwich. The same holds for the downward iodide-ion layer. This can be depicted as:

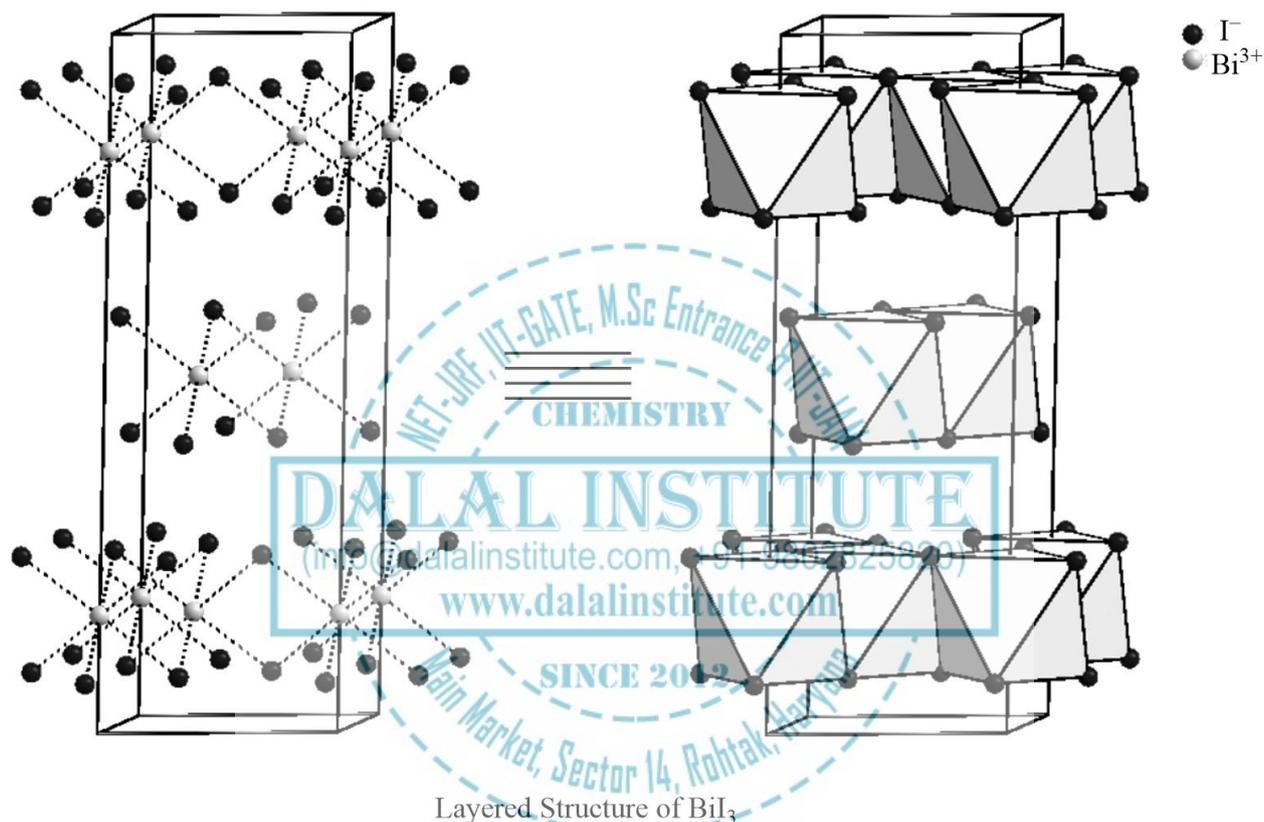


Figure 14. The layered lattice of BiI_3 crystal system.

4. The number of formula units present per unit cell of bismuth iodide is six.
5. The third side of the trigonal (hexagonal) lattice is approximately three times to that of the remaining two sides which are equal to each other.

The BiI_3 crystal belongs to a class of layered lattices of heavy metal semiconductors with fascinating anisotropic optical and electronic properties. The single crystals and thin films and of bismuth iodide have been studied for X-ray imaging due to the relatively wide bandgap, high mass density and high atomic numbers of the constituent elements. It can also be used as hard radiation detectors. Moreover, because BiI_3 can be processed in the solution phase; cost-efficient, large-scale device fabrication could be facilitated.

➤ 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.

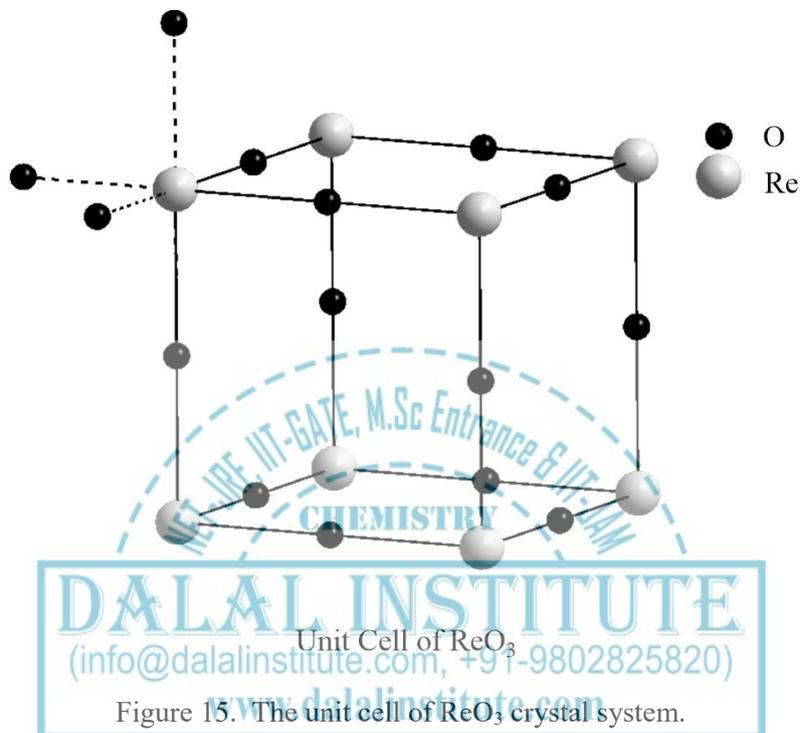


Figure 15. The unit cell of ReO_3 crystal system.

The main features of this crystal structure are as follows:

1. Rhenium oxide crystallizes with a primitive cubic unit cell. Re atoms are present at all the corners while the oxygen atoms are situated at the center of 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 the rhenium atom is octahedral and of the 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 structure is similar to perovskite (ABO_3), just the large A cation is 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 optical, glass and ceramic based other devices.

➤ **Mn₂O₃**

Manganese oxide is an inorganic solid of manganese and oxygen. Mn₂O₃ generally exists in two forms, α -Mn₂O₃ and γ -Mn₂O₃. The heating of MnO₂ in the air at below 800 °C produces α -Mn₂O₃ (higher temperatures produce Mn₃O₄) while γ -Mn₂O₃ can be produced by oxidation followed by dehydration of Mn(OH)₂. The crystal structure of the two forms can be discussed as:

1. **α -Mn₂O₃**: The unit cell of α -Mn₂O₃ crystal form is shown below.

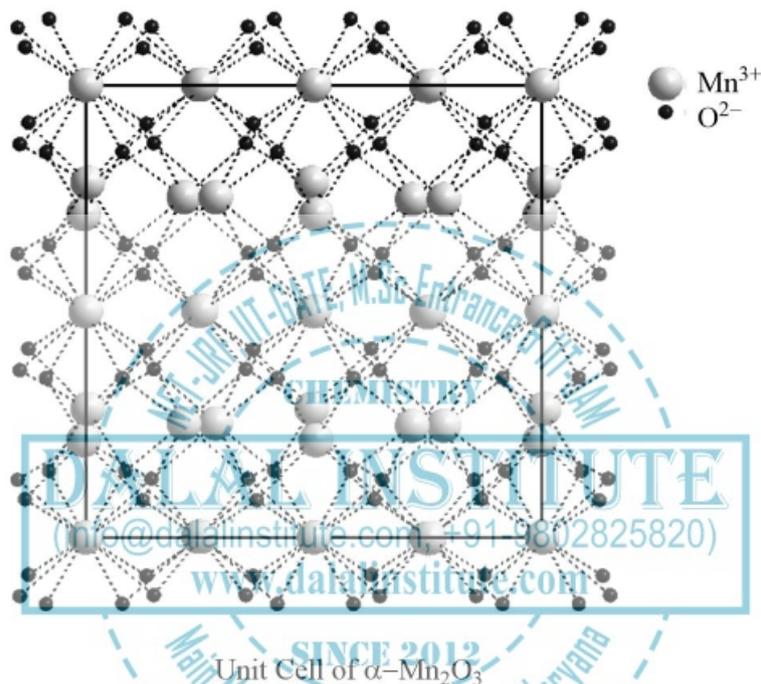


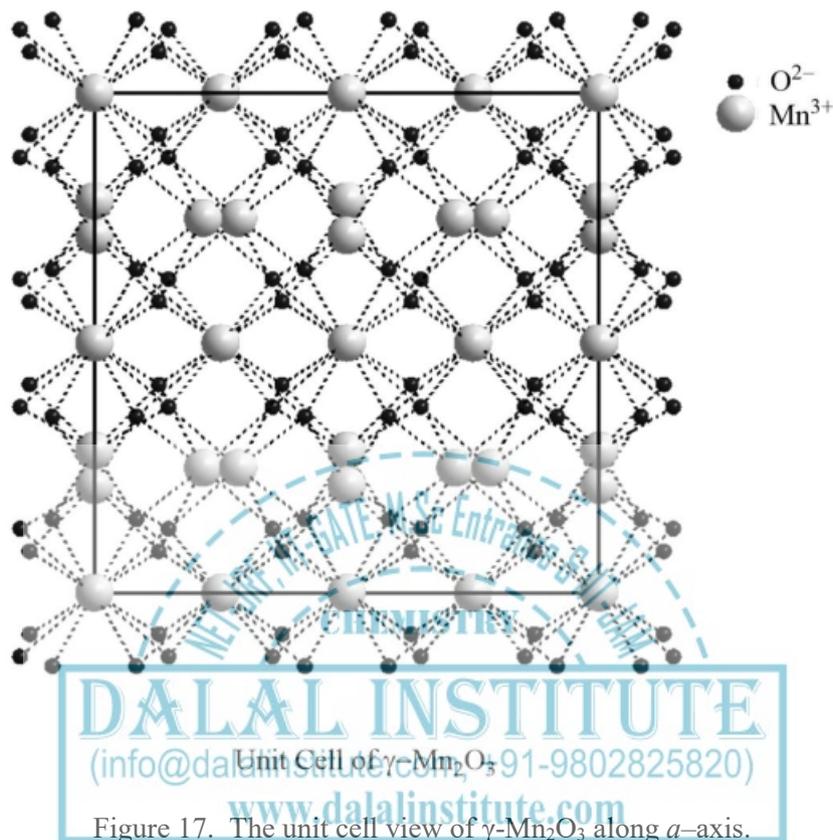
Figure 16. The unit cell view of α -Mn₂O₃ along *a*-axis.

The main features of this crystal structure are as follows:

1. The crystallization of α -Mn₂O₃ takes place in an orthorhombic lattice with five different octahedral coordinative environments around manganese ions.
2. Each Mn³⁺ ion is surrounded by six oxide ions while each O²⁻ ion is coordinated by four metal ions. The coordinating geometry of all five types of manganese ions is distorted octahedra and of all the six types of oxide ions are distorted tetrahedral in nature. Therefore, the coordination number ratio of Mn³⁺ and O²⁻ is 6:4.
3. The number of formula units present per unit cell is 16.
4. α -Mn₂O₃ has the cubic bixbyite structure, which is an example of a C-type rare earth sesquioxide.

The bandgap emission of nanocrystalline α -Mn₂O₃ is important due to their applications as ultra-violet (UV) emitters.

2. $\gamma\text{-Mn}_2\text{O}_3$: The unit cell of $\gamma\text{-Mn}_2\text{O}_3$ form is shown below.



The main features of this crystal structure are as follows:

1. The crystallization of $\gamma\text{-Mn}_2\text{O}_3$ takes place in a cubic lattice with two different octahedral coordinative environments around manganese ions.
2. Each Mn^{3+} ion is surrounded by six oxide ions while each O^{2-} ion is coordinated by four metal ions. The first type coordinating geometry around manganese ions is distorted octahedra while the second type coordinating geometry around manganese ion is a perfect octahedron. However, only one kind of coordinative environment around oxide ions is observed with a distorted tetrahedral symmetry in nature. Therefore, the coordination number ratio of Mn^{3+} and O^{2-} is 6:4.
3. The number of formula units present per unit cell is 16.
4. $\gamma\text{-Mn}_2\text{O}_3$ has a structure related to the spinel structure of Mn_3O_4 where the oxide ions are cubic close-packed. This is similar to the relationship between $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 .

$\gamma\text{-Mn}_2\text{O}_3$ is ferrimagnetic with a Neel temperature of 39 K and nanoparticle form has found a great deal of interest for applications in biology and material science.

➤ **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.

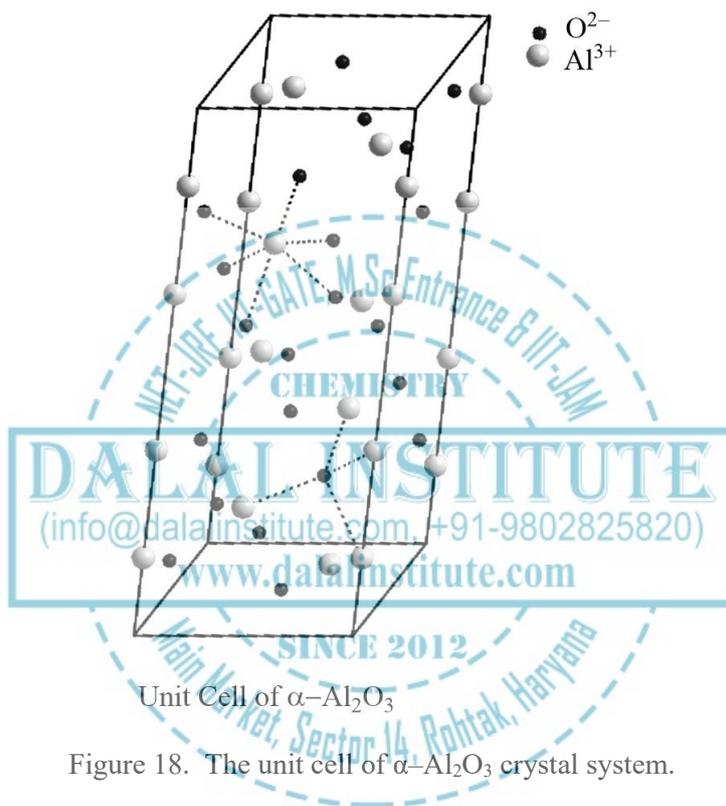


Figure 18. The unit cell of $\alpha\text{-Al}_2\text{O}_3$ crystal system.

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.

➤ **Perovskite**

The perovskite is an oxide mineral of calcium titanium with formula CaTiO_3 . The mineral was found by Gustav Rose in the Ural Mountains of Russia in 1839 and is also named after a Russian mineralogist Lev Perovskite. The unit cell of perovskite is shown below.

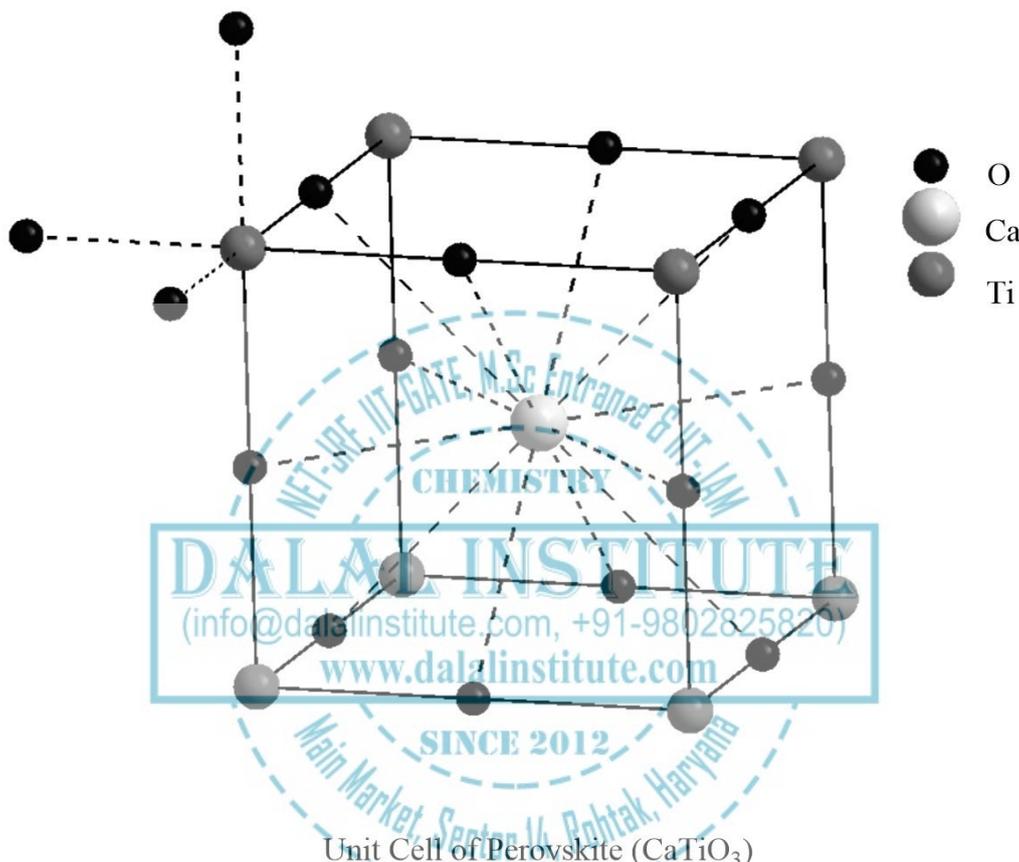
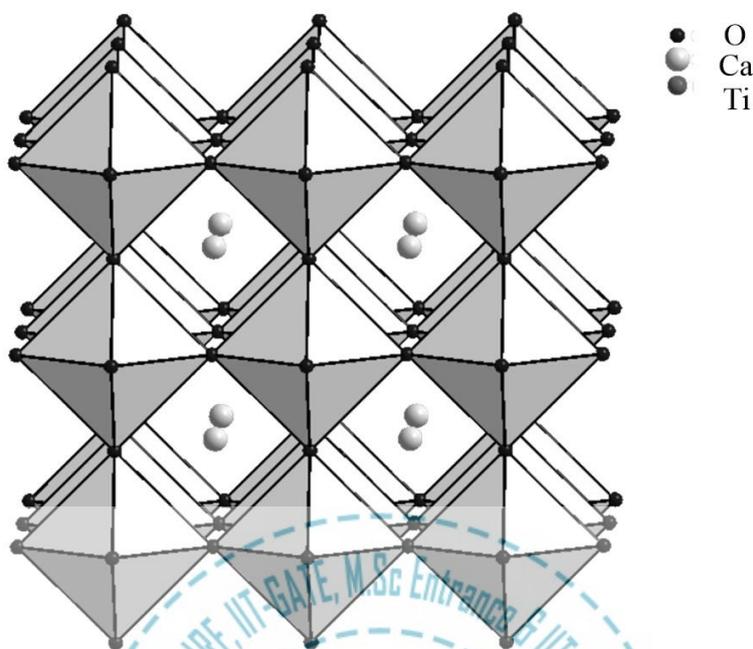


Figure 19. The unit cell of the perovskite crystal system.

The main features of this crystal structure are as follows:

1. CaTiO_3 crystallizes with a cubic unit cell in which Ti atoms are present at all the corners while the oxygen atoms are situated center of at all the edges. The large Ca^{2+} cation is present at the center of the unit cell.
2. Each Ti atom is surrounded by six oxygen atoms while each O atom is coordinated by two titanium atoms. The coordinating geometry of rhenium atom is octahedral and of oxygen atom is linear in nature. Therefore, the coordination number ratio of Ti and O is 6:2. Furthermore, the calcium cation is surrounded by twelve oxygens.
3. The octahedron units, TiO_6 , share corners to form the 3-dimensional structure.



Three Dimensional structure of CaTiO_3

Figure 20. Three-dimensional structure of perovskite crystal system.

4. The number of formula units present per unit cell is one.
5. The structure of perovskite is adopted by many other oxides which have the ABO_3 formula.
6. The relative size different ions, required for stability of the cubic lattice are pretty much inflexible; therefore, very slight distortion and buckling can generate many lower-symmetry distorted versions, with coordination numbers of B cations, A cations or both are decreased. The Tilting of BO_6 polyhedra reduces the coordination of an undersized cation A from twelve to as low as eight. Conversely, off-centering of an undersized cation B within its polyhedral unit allows it to attain a stable bonding pattern. The resulting electric dipole is accountable for the ferroelectricity possessed and shown by some perovskites like BaTiO_3 which are distorted in profile.
7. The tetragonal and orthorhombic crystal phases are the most common non-cubic types.
8. The possibility of disordered and ordered variants results in some complex perovskite kinds which contain two dissimilar B-site cations.

Perovskite structures possess many intriguing and interesting properties from theoretical as well as the application viewpoint. Massive magnetoresistance, superconductivity, ferroelectricity, charge ordering, high thermos-power, spin-dependent transport and the interplay of magnetic, structural and transport properties are the most commonly observed features in this class. These compounds are used as catalyst electrodes and sensors in some types of fuel cells and are good candidates for spintronics applications and memory devices.

➤ **Ilmenite**

Ilmenite is an oxide mineral of titanium and iron with formula FeTiO_3 . It is a weakly magnetic steel-gray or black solid material. The unit cell of Ilmenite is shown below.

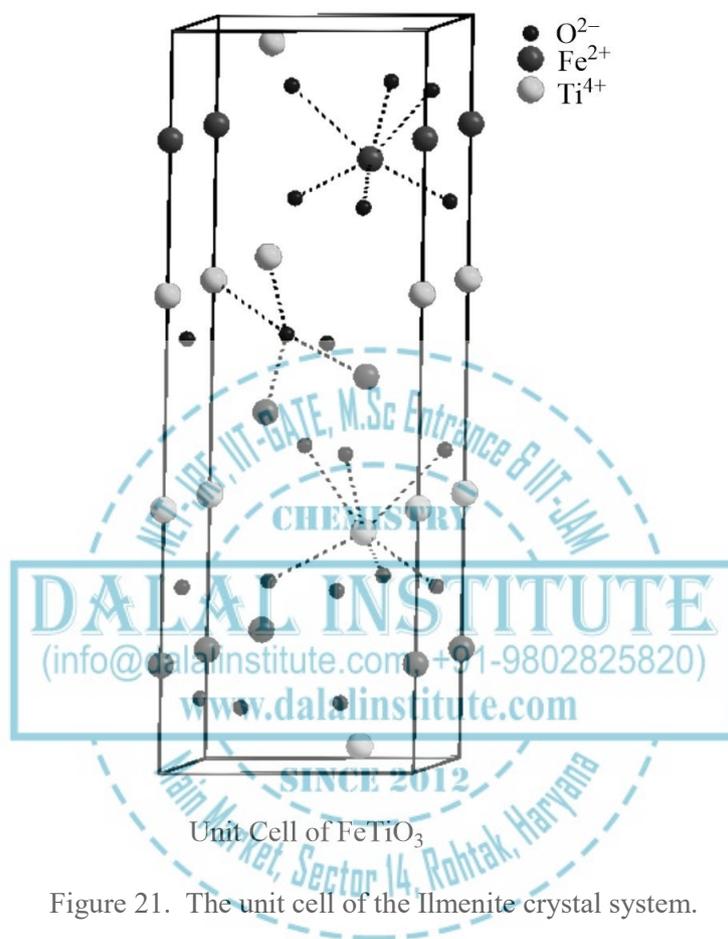


Figure 21. The unit cell of the Ilmenite crystal system.

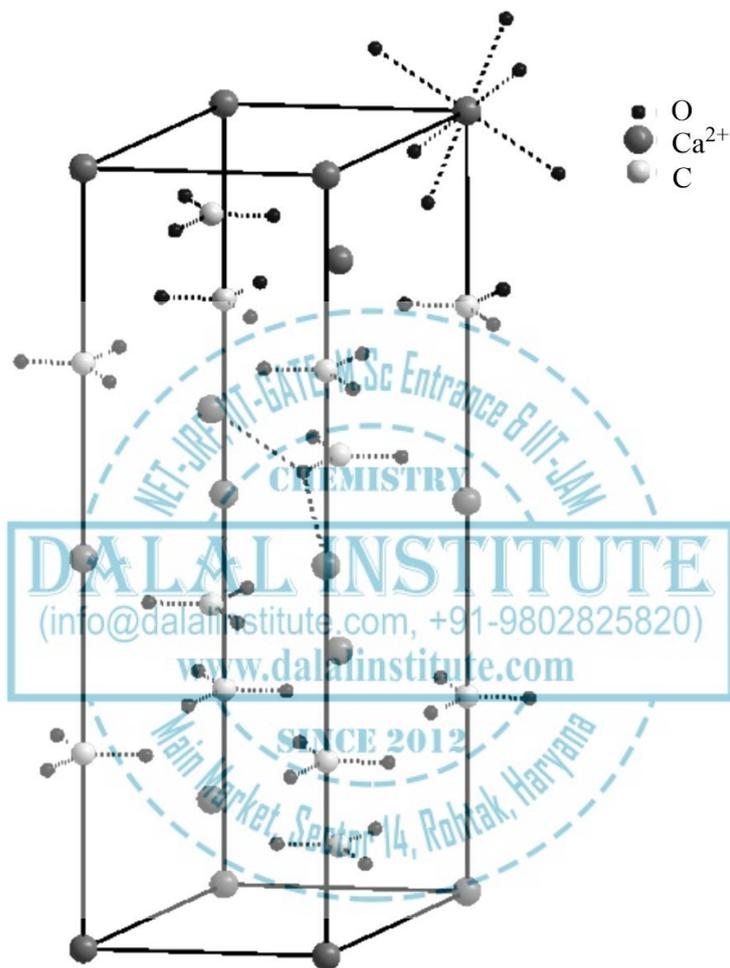
The main features of this crystal structure are as follows:

1. FeTiO_3 crystallizes in a trigonal crystal system which can be considered as an ordered imitative of the corundum structure. In corundum, all cations are the same but in FeTiO_3 , the Fe^{2+} and Ti^{4+} ions occupy alternating layers, perpendicular to the trigonal c -axis. Ilmenite is paramagnetic due to high spin ferrous centers.
2. Each Ti^{4+} and Fe^{2+} ion is surrounded by six oxide ions while each O^{2-} atom is coordinated by two Ti^{4+} and two Fe^{2+} ions. The coordinating geometry of titanium ion and ferrous ion is distorted octahedral and of oxide ion is distorted tetrahedral in nature. Hence, the coordination number ratio of Ti^{4+} , Fe^{2+} and O^{2-} ions is 6:6:4.

As far as the commercial importance is concerned, the ilmenite is the best ore for Ti. It is the primary source of TiO_2 , which is used in fabrics, paints, paper, food, plastics, cosmetics and sunscreen.

➤ **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 of Ilmenite is shown below.



Unit Cell Of Calcite (CaCO_3)

Figure 21. The unit cell of calcite crystal.

The main features of this crystal structure are as follows:

1. 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} .



❖ Problems

- Q 1. 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.
- Q 2. Draw and discuss the crystal structure of fluorite.
- Q 3. How does the Na_2O structure differ from the crystal structure of CaF_2 ?
- Q 4. What is rutile? Explain its structure.
- Q 5. Give five points differentiating the antirutile structure from the rutile one.
- Q 6. Define the term layered lattice. Draw and discuss two examples in detail.
- Q 7. Draw and discuss the crystal structure of β -cristobalite.
- Q 8. How does the crystal structure of ReO_3 differ from the perovskite? Explain with suitable diagram.
- Q 9. Compare the crystal structures of ilmenite and corundum.
- Q 10. What is calcite? Draw and discuss its crystal structure.

❖ Bibliography

- [1] J. D. Lee, *Concise Inorganic Chemistry*, Chapman & Hall, New York, USA, 1994.
- [2] B. R. Puri, L. R. Sharma, K. C. Kalia, *Principals of Inorganic Chemistry*, Milestone Publishers, Delhi, India, 2012.
- [3] J. E. Huheey, E. A. Keiter, R. L. Keiter, *Inorganic Chemistry: Principals of Structure and Reactivity*, HarperCollins College Publishers, New York, USA, 1993.
- [4] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, London, UK, 1975.
- [5] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, John Wiley & Sons, New Jersey, USA, 1999.
- [6] G. Raj, *Advanced Inorganic Chemistry Vol-1*, Krishna Prakashan Media, Uttar Pradesh, India, 2008.
- [7] G. S. Girolami, *X-ray Crystallography*, University Science Books, California, USA, 2016.

LEGAL NOTICE

This document is an excerpt from the book entitled “A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal”, and is the intellectual property of the Author/Publisher. The content of this document is protected by international copyright law and is valid only for the personal preview of the user who has originally downloaded it from the publisher’s website (www.dalalinstitute.com). Any act of copying (including plagiarizing its language) or sharing this document will result in severe civil and criminal prosecution to the maximum extent possible under law.



This is a low resolution version only for preview purpose. If you want to read the full book, please consider buying.

Buy the complete book with TOC navigation, high resolution images and no watermark.

Home

CLASSES

NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

BOOKS

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

[READ MORE](#)

VIDEOS

Video Lectures

Want video lectures in chemistry for CSIR UGC - NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

[READ MORE](#)

Home: <https://www.dalalinstitute.com/>

Classes: <https://www.dalalinstitute.com/classes/>

Books: <https://www.dalalinstitute.com/books/>

Videos: <https://www.dalalinstitute.com/videos/>

Location: <https://www.dalalinstitute.com/location/>

Contact Us: <https://www.dalalinstitute.com/contact-us/>

About Us: <https://www.dalalinstitute.com/about-us/>

Postgraduate Level Classes (NET-JRF & IIT-GATE)

Admission

[Regular Program](#)

[Test Series](#)

[Distance Learning](#)

[Result](#)

Undergraduate Level Classes (M.Sc Entrance & IIT-JAM)

Admission

[Regular Program](#)

[Test Series](#)

[Distance Learning](#)

[Result](#)

A Textbook of Inorganic Chemistry – Volume 1

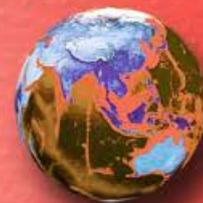
“A Textbook of Inorganic Chemistry – Volume 1 by Mandeep Dalal” is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.

[READ MORE](#)

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

[Sign Up](#)

International
Edition



A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

CHAPTER 1	11
Stereochemistry and Bonding in Main Group Compounds:.....	11
❖ VSEPR Theory	11
❖ $d\pi-p\pi$ Bonds	23
❖ Bent Rule and Energetic of Hybridization.....	28
❖ Problems	42
❖ Bibliography	43
CHAPTER 2	44
Metal-Ligand Equilibria in Solution:.....	44
❖ Stepwise and Overall Formation Constants and Their Interactions	44
❖ Trends in Stepwise Constants.....	46
❖ Factors Affecting Stability of Metal Complexes with Reference to the Nature of Metal Ion and Ligand.....	49
❖ Chelate Effect and Its Thermodynamic Origin.....	56
❖ Determination of Binary Formation Constants by pH-metry and Spectrophotometry.....	63
❖ Problems	68
❖ Bibliography	69
CHAPTER 3	70
Reaction Mechanism of Transition Metal Complexes – I:.....	70
❖ Inert and Labile Complexes.....	70
❖ Mechanisms for Ligand Replacement Reactions	77
❖ Formation of Complexes from Aquo Ions.....	82
❖ Ligand Displacement Reactions in Octahedral Complexes- Acid Hydrolysis, Base Hydrolysis....	86
❖ Racemization of Tris Chelate Complexes	89
❖ Electrophilic Attack on Ligands	92
❖ Problems	94
❖ Bibliography	95

CHAPTER 4	96
Reaction Mechanism of Transition Metal Complexes – II:	96
❖ Mechanism of Ligand Displacement Reactions in Square Planar Complexes.....	96
❖ The Trans Effect.....	98
❖ Theories of Trans Effect.....	103
❖ Mechanism of Electron Transfer Reactions – Types; Outer Sphere Electron Transfer Mechanism and Inner Sphere Electron Transfer Mechanism.....	106
❖ Electron Exchange.....	117
❖ Problems.....	121
❖ Bibliography.....	122
CHAPTER 5	123
Isopoly and Heteropoly Acids and Salts:	123
❖ Isopoly and Heteropoly Acids and Salts of Mo and W: Structures of Isopoly and Heteropoly Anions	123
❖ Problems.....	152
❖ Bibliography.....	153
CHAPTER 6	154
Crystal Structures:	154
❖ Structures of Some Binary and Ternary Compounds Such as Fluorite, Antifluorite, Rutile, Antirutile, Cristobalite, Layer Lattices - CdI ₂ , BiI ₃ ; ReO ₃ , Mn ₂ O ₃ , Corundum, Pervoskite, Ilmenite and Calcite.....	154
❖ Problems.....	178
❖ Bibliography.....	179
CHAPTER 7	180
Metal-Ligand Bonding:	180
❖ Limitation of Crystal Field Theory.....	180
❖ Molecular Orbital Theory – Octahedral, Tetrahedral or Square Planar Complexes.....	184
❖ π -Bonding and Molecular Orbital Theory	198
❖ Problems.....	212
❖ Bibliography.....	213

CHAPTER 8	214
Electronic Spectra of Transition Metal Complexes:	214
❖ Spectroscopic Ground States	214
❖ Correlation and Spin-Orbit Coupling in Free Ions for 1st Series of Transition Metals.....	243
❖ Orgel and Tanabe-Sugano Diagrams for Transition Metal Complexes ($d^1 - d^9$ States).....	248
❖ Calculation of Dq , B and β Parameters	280
❖ Effect of Distortion on the d -Orbital Energy Levels	300
❖ Structural Evidence from Electronic Spectrum	307
❖ Jahn-Teller Effect	312
❖ Spectrochemical and Nephelauxetic Series	324
❖ Charge Transfer Spectra	328
❖ Electronic Spectra of Molecular Addition Compounds.....	336
❖ Problems	340
❖ Bibliography	341
CHAPTER 9	342
Magnetic Properties of Transition Metal Complexes:	342
❖ Elementary Theory of Magneto-Chemistry	342
❖ Guoy's Method for Determination of Magnetic Susceptibility	351
❖ Calculation of Magnetic Moments	354
❖ Magnetic Properties of Free Ions.....	359
❖ Orbital Contribution: Effect of Ligand-Field	362
❖ Application of Magneto-Chemistry in Structure Determination	370
❖ Magnetic Exchange Coupling and Spin State Cross Over	375
❖ Problems	384
❖ Bibliography	385
CHAPTER 10	386
Metal Clusters:	386
❖ Structure and Bonding in Higher Boranes.....	386
❖ Wade's Rules.....	401

❖ Carboranes	407
❖ Metal Carbonyl Clusters- Low Nuclearity Carbonyl Clusters.....	412
❖ Total Electron Count (TEC)	417
❖ Problems	424
❖ Bibliography	425
CHAPTER 11	426
Metal-II Complexes:	426
❖ Metal Carbonyls: Structure and Bonding	426
❖ Vibrational Spectra of Metal Carbonyls for Bonding and Structure Elucidation.....	439
❖ Important Reactions of Metal Carbonyls.....	446
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes.....	450
❖ Tertiary Phosphine as Ligand.....	463
❖ Problems	469
❖ Bibliography	470
INDEX.....	471



Mandeep Dalal

(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)

Founder & Director, Dalal Institute

Contact No: +91-9802825820

Homepage: www.mandeepdalal.com

E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-0-0



9 788193 872000 >

MRP: Rs 800.00

D DALAL
INSTITUTE

Main Market, Sector 14, Rohtak, Haryana 124001, India

(+91-9802825820, info@dalalinstitute.com)

www.dalalinstitute.com