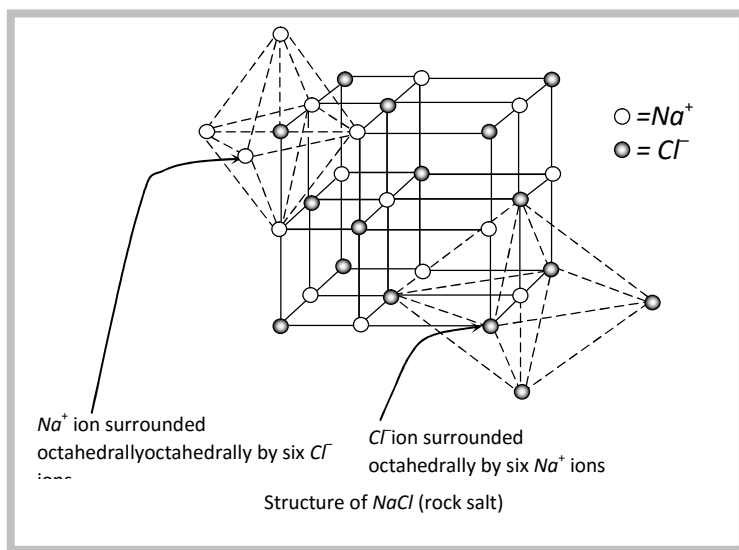


## Crystal structures and Method of determination.

Ionic compounds consist of positive and negative ions arranged in a manner so as to acquire minimum potential energy (maximum stability). To achieve the maximum stability, ions in a crystal should be arranged in such a way that forces of attraction are maximum and forces of repulsion are minimum. Hence, for maximum stability the oppositely charged ions should be as close as possible to one another and similarly charged ions as far away as possible from one another. Among the two ions constituting the binary compounds, the larger ions (usually anions) form a close-packed arrangement (hcp or ccp) and the smaller ions (usually cations) occupy the interstitial voids. Thus in every ionic compound, positive ions are surrounded by negative ions and vice versa. Normally each ion is surrounded by the largest possible number of oppositely charged ions. This number of oppositely charged ions surrounding each ion is termed its coordination number.

Classification of ionic structures: In the following structures, a black circle would denote an anion and a white circle would denote a cation. In any solid of the type  $A_xB_y$  the ratio of the coordination number of A to that of B would be  $y : x$ .

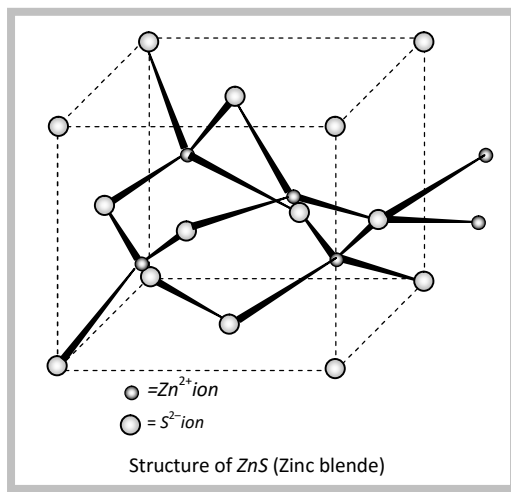
(1) Rock salt structure: The NaCl structure is composed of  $Na^+$  and  $Cl^-$ . The no. of  $Na^+$  ions is equal to that of  $Cl^-$ . The radii of  $Na^+$  and  $Cl^-$  are 95 pm and 181 pm respectively  $\frac{r_{Na^+}}{r_{Cl^-}} = \frac{95 \text{ pm}}{181 \text{ pm}} = 0.524$ . The radius ratio of 0.524 for NaCl suggests an octahedral voids. Chloride is forming a fcc unit cell in which  $Na^+$  is in the octahedral voids. The coordination number of  $Na^+$  is 6 and therefore that of  $Cl^-$  would also be 6. Moreover, there are 4  $Na^+$  ions and 4  $Cl^-$  ions per unit cell. The formula is  $Na_4Cl_4$  i.e., NaCl. The other substances having this kind of a structure are halides of all alkali metals except cesium, halides and oxides of all alkaline earth metals except beryllium oxide.



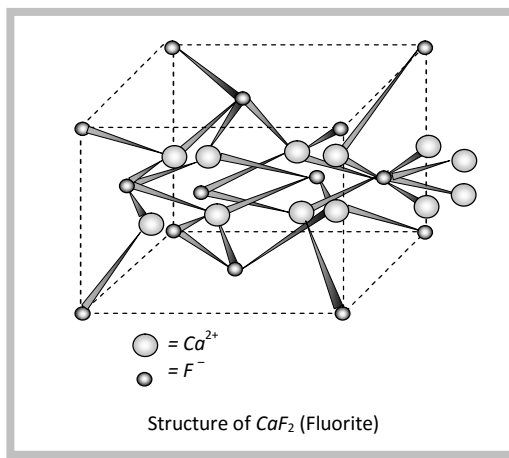
(2) Zinc blende structure: Sulphide ions are face centered and zinc is present in alternate tetrahedral voids. Formula is  $Zn_4S_4$ , i.e., ZnS. Coordination number of Zn is 4 and that of sulphide is also 4. Other substance that exists in this kind of a structure is BeO.

The zinc sulphide crystals are composed of equal no. of  $Zn^{+2}$  and  $S^{2-}$  ions. The radii of two ions ( $Zn^{+2} = 74 pm$  and  $S^{2-} = 184 pm$ ) led to the radius ratio ( $r^+ / r^-$ ) as 0.40 which suggests a tetrahedral arrangement

$$\frac{r_{Zn^{+2}}}{r_{S^{2-}}} = \frac{74 pm}{184 pm} = 0.40$$



(3) Fluorite structure: Calcium ions are face centered and fluoride ions are present in all the tetrahedral voids. There are four calcium ions and eight fluoride ions per unit cell. Therefore the formula is  $Ca_4F_8$ , (i.e.  $CaF_2$ ). The coordination number of fluoride ions is four (tetrahedral voids) and thus the coordination number of calcium ions is eight. Other substances which exist in this kind of structure are  $UO_2$  and  $ThO_2$ .



(4) Anti-fluorite structure: Oxide ions are face centered and lithium ions are present in all the tetrahedral voids. There are four oxide ions and eight lithium ions per unit cell. As it can be seen, this unit cell is just the reverse of fluorite structure, in the sense that, the position of cations and anions is interchanged. Other substances which exist in this kind of a structure are  $Na_2O$ ,  $K_2O$  and  $Rb_2O$ .

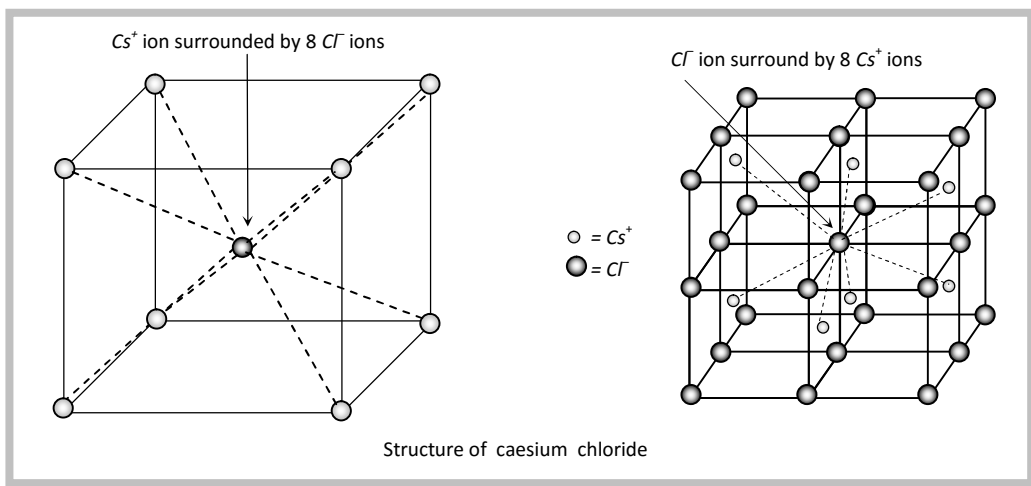
(5) Spinel and inverse spinel structure: Spinel is a mineral ( $MgAl_2O_4$ ). Generally they can be represented as  $M^{2+}M_2^{3+}O_4$ . Where  $M^{2+}$  is present in one-eighth of tetrahedral voids in a fcc lattice of oxide ions and  $M^{3+}$  present in half of the octahedral voids.  $M^{2+}$  is usually Mg, Fe, Co, Ni, Zn and Mn,  $M^{3+}$  is generally Al, Fe, Mn, Cr and Rh. e.g.,  $ZnAl_2O_4$ ,  $Fe_3O_4$ ,  $FeCr_2O_4$  etc.

(6) Cesium halide structure: Chloride ions are primitive cubic while the cesium ion occupies the center of the unit cell. There is one chloride ion and one cesium ion per unit cell. Therefore the formula is CsCl. The coordination number of cesium is eight and that of chloride is also eight. Other substances which exist in this kind of a structure are all halides of cesium.

The  $CsCl$  crystal is composed of equal no. of  $Cs^+$  and  $Cl^-$  ions. The radii of two ions ( $r_{Cs^+} = 160 pm$  and  $r_{Cl^-} = 181 pm$ ) led to radius ratio of  $r_{Cs^+}$  to  $r_{Cl^-}$  as 0.884

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{160 pm}{181 pm} = 0.884$$

Suggests a body centered cubic structure cubic structure having a cubic hole.



(7) Corundum structure: The general formula of compounds crystallizing in corundum structure is  $Al_2O_3$ . The closest packing is that of anions (oxide) in hexagonal primitive lattice and two-third of the octahedral voids are filled with trivalent cations. e.g.,  $Fe_2O_3$ ,  $Al_2O_3$  and  $Cr_2O_3$ .

(8) Pervoskite structure: The general formula is  $ABO_3$ . One of the cation is bivalent and the other is tetravalent. e.g.,  $CaTiO_3$ ,  $BaTiO_3$ . The bivalent ions are present in primitive cubic lattice with oxide ions on the centers of all six square faces. The tetravalent cation is in the center of the unit cell occupying octahedral void.

Note: On applying high pressure, NaCl structure having 6:6 coordination number changes to CsCl structure having 8:8 coordination number similarly, CsCl having 8:8 coordination number on heating to 760 K changes to NaCl structure having 6:6 coordination number.

$NaCl$	$\xrightarrow{\text{Pressure}}$	$CsCl$
6 : 6 Co – orditnation number	$\xleftarrow{\text{Temp.}}$	8 : 8 Co – orditnation number

Depending upon the relative number of positive and negative ions present in ionic compounds, it is convenient to divide them into groups like AB, AB<sub>2</sub>, AB<sub>3</sub>, etc. Ionic compounds of the type AB and AB<sub>2</sub> are discussed below.

S. No.	Crystal Structure	Brief description	Examples	Co-ordination number	Number of formula units per unit cell
1.	Type AB Rock salt (NaCl) type	It has fcc arrangement in which $Cl^-$ ions occupy the corners and face centers of a cube while $Na^+$ ions are present at the body and edge of centers.	Halides of Li, Na, K, Rb, AgF, AgBr, NH <sub>4</sub> Cl, NH <sub>4</sub> Br, NH <sub>4</sub> I etc.	$Na^+ = 6$ $Cl^- = 6$	4
2.	Zinc blende (ZnS) type	It has ccp arrangement in which $S^{2-}$ ions form fcc and each $Zn^{2+}$ ion is surrounded tetrahedrally by four $S^{2-}$ ions and vice versa.	$CuCl$ , $CuBr$ , $CuI$ , $AgI$ , $BeS$	$Zn^{2+} = 4$ $S^{2-} = 4$	4
3.	Type AB <sub>2</sub>	It has arrangement in which	$BaF_2$ , $BaCl_2$ , $SrF_2$	$Ca^{2+} = 8$	4

	Fluorite (CaF <sub>2</sub> ) type	$Ca^{2+}$ ions form fcc with each $Ca^{2+}$ ions surrounded by $8F^{-}$ ions and each $F^{-}$ ions by $4Ca^{2+}$ ions.	$SrCl_2, CdF_2, PbF_2$	$F^{-} = 4$	
4.	Antifluorite type	Here negative ions form the ccp arrangement so that each positive ion is surrounded by 4 negative ions and each negative ion by 8 positive ions	$Na_2O$	$Na^{+} = 4$ $O^{2-} = 8$	4
5.	Caesium chloride (CsCl) type	It has the bcc arrangement with $Cs^{+}$ at the body center and $Cl^{-}$ ions at the corners of a cube or vice versa.	$CsCl, CsBr, CsI, CsCN,$ $TlCl, TlBr, TlI$ and $TlCN$	$Cs^{+} = 8$ $Cl^{-} = 8$	1

(iii) Crystal structure of some metals at room temperature and pressure:

