



Ionic Solids

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In ionic solids, cation being smaller is **situated at the void position**

Rules for stable configuration

No Rattling

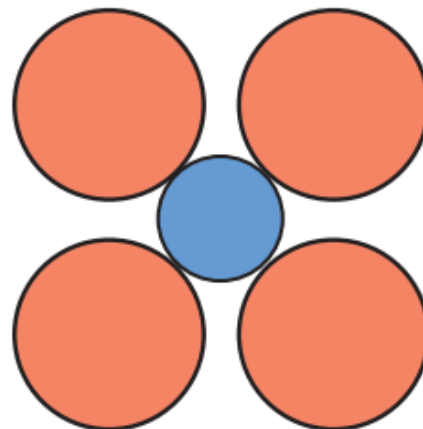
The cation should not be smaller than the void formed by the anions

Cation size larger than the void

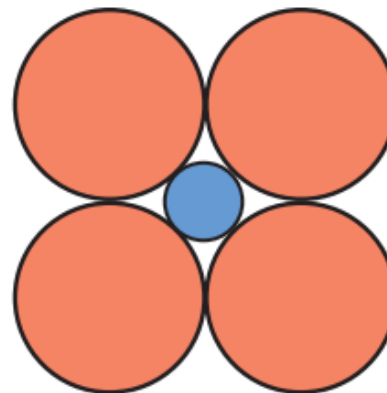
The cation should be larger than the void so that the anions do not touch each other

Choose the largest coordination possible

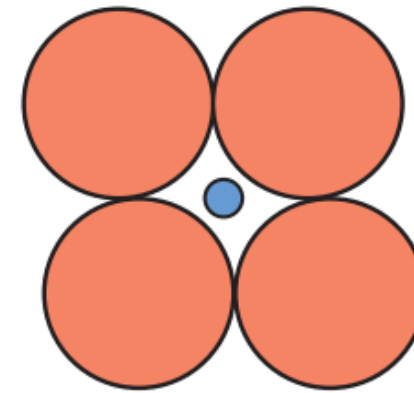
Largest coordination gives the best possible packing



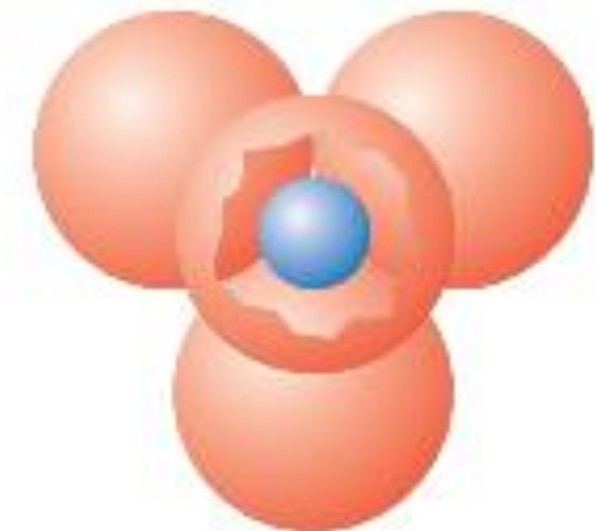
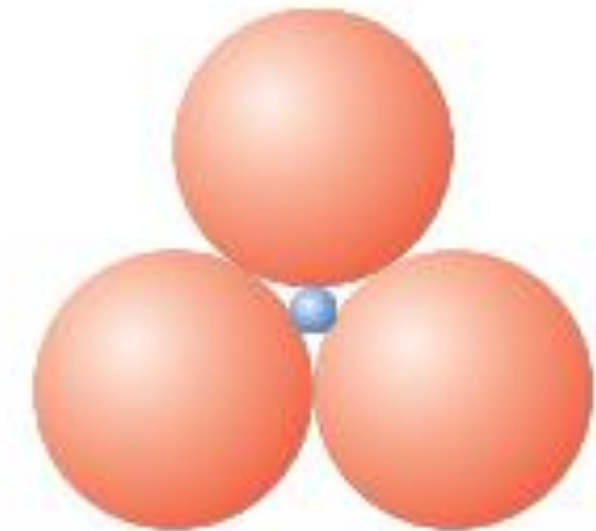
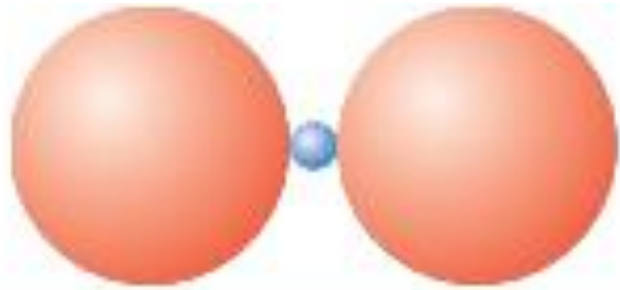
Stable



Stable

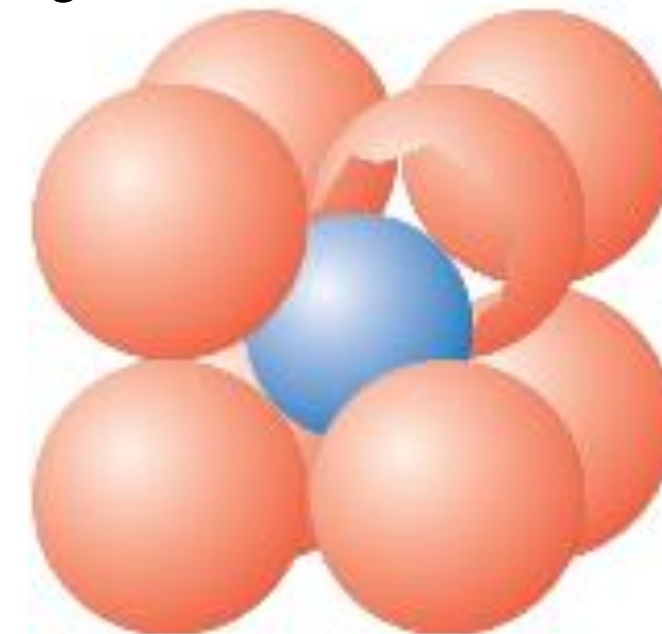
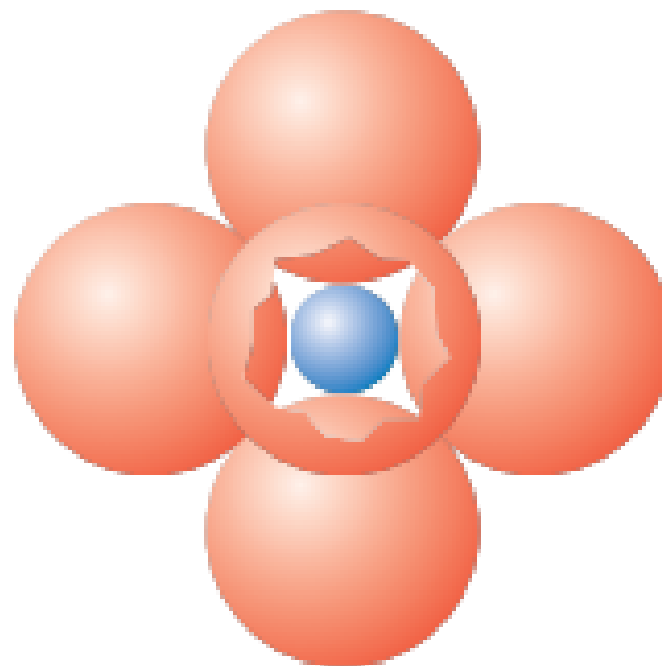


Unstable



Ligacy	r_c / r_a	Configuration	E.g.	
				r_c / r_a
2	0 – 0.155	Linear		
3	0.155 – 0.225	Triangular		
4	0.225 – 0.414	Tetrahedral		
6	0.414 – 0.732	Octahedral	NaCl	0.54
8	0.732 – 1.0	Cubic	CsCl	0.91
12	1.0	FCC or HCP		

The ratio r_c / r_a (radius of cation : radius of anion) determines the coordination number / Ligacy for the cation → the local packing



1. AB type (same no. of anions and cations)

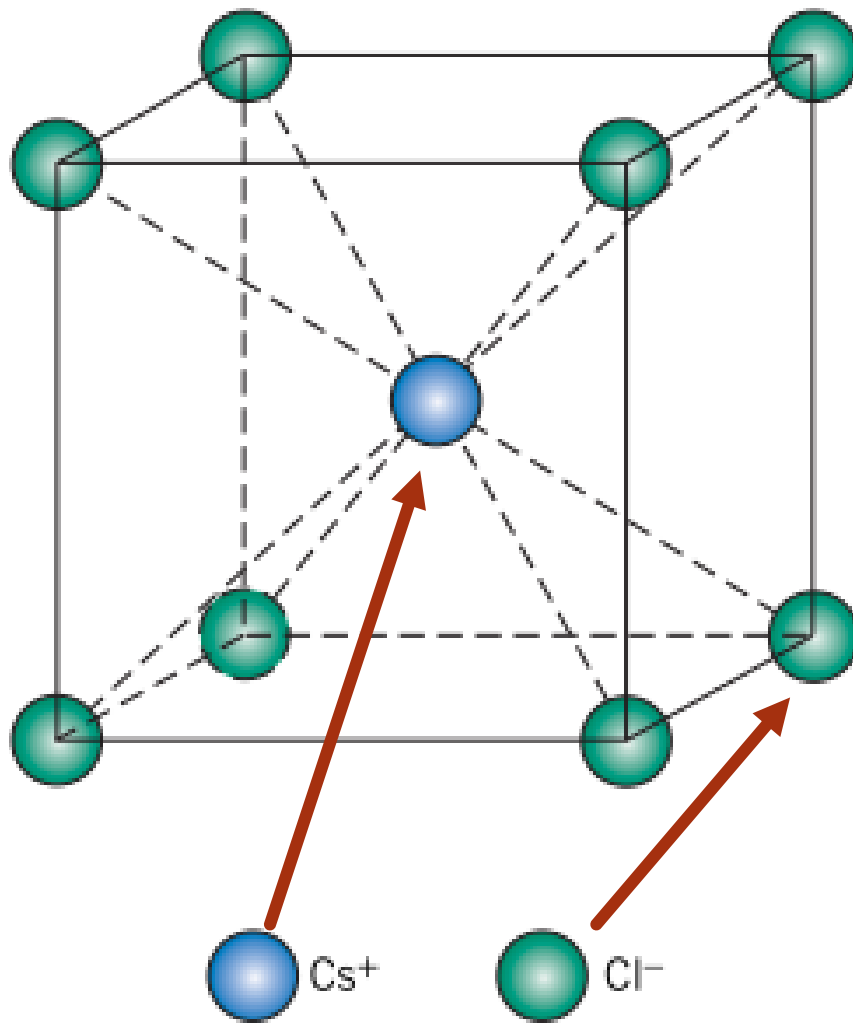
A - cation, B - anion

2. ABO_3 type - Perovskite structure

3. AB_2O_4 type - Spinel structure

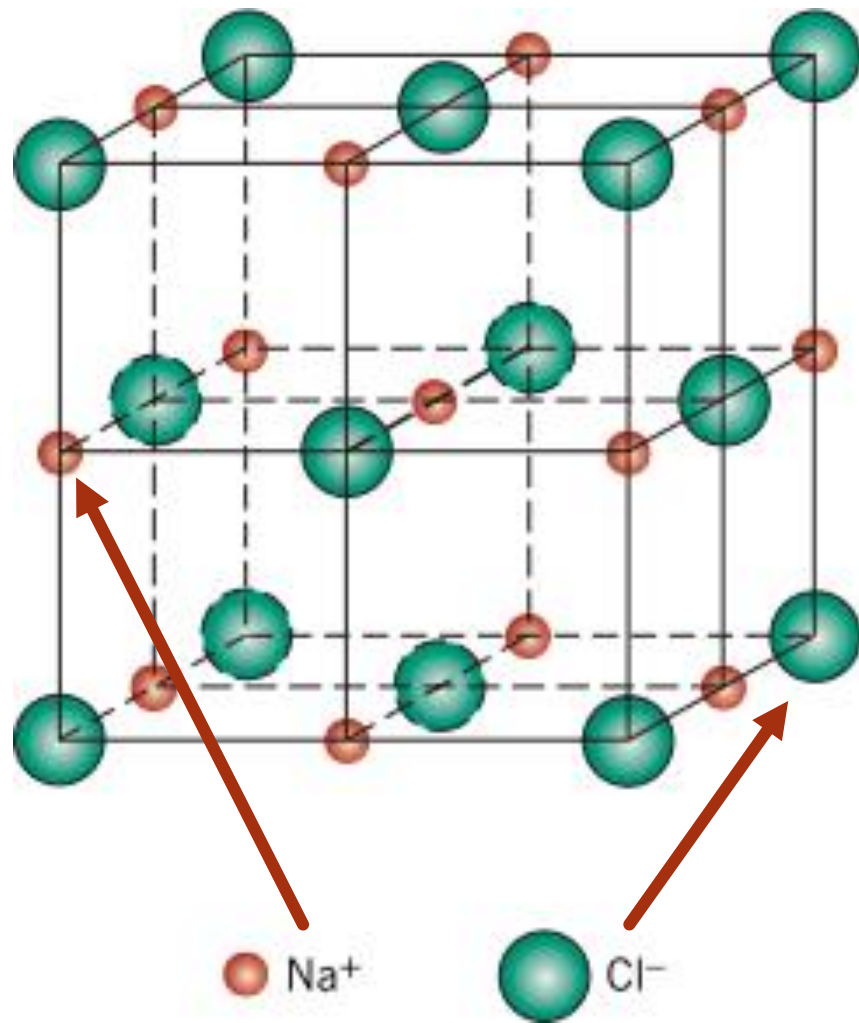
A/B – cation, O-oxygen ion (anion)

CsCl crystal structure



- Lattice type: Primitive cubic lattice.
- Void type: Cubic type
- No. of anion and cations: 1
- Relation a and R : $a\sqrt{3} = 2R_a + 2R_c$
- Motif: Anions (A): 0 0 0, Cations (B): $\frac{1}{2} \frac{1}{2} \frac{1}{2}$
- 100% occupancy of sites according to the stoichiometry.
- Examples: Halides such as CsCl, AgI, AgBr, CsI, LiMg etc.

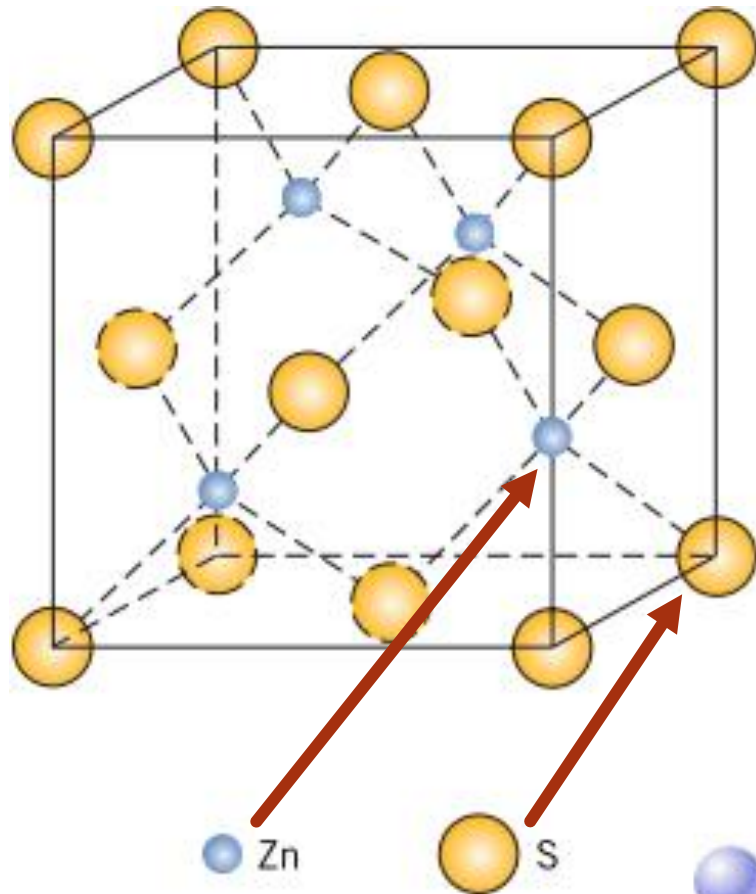
NaCl crystal structure



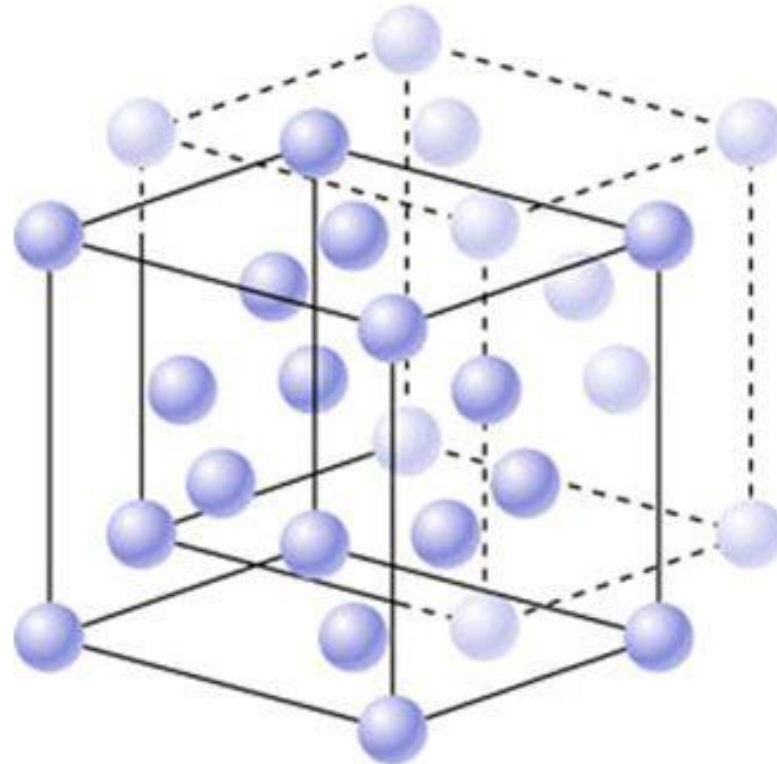
- Lattice type: FCC lattice.
- Void type: Octahedral.
- No. of anion and cations: 4
- Relation a and R : $a = 2 R_a + 2 R_c$
- Motif: Anions (A): 0 0 0, Cations (B): $\frac{1}{2}$ 0 0
- Anions (A) form the cation sub lattice with FCC structure.
- Cations (B) fill the octahedral sites.
- 100% occupancy of sites according to the stoichiometry since there will be one octahedral site per anion.
- Examples NaCl, MgO, NiO, LiF, TiN, FeO etc.

AX or AB type ionic crystals

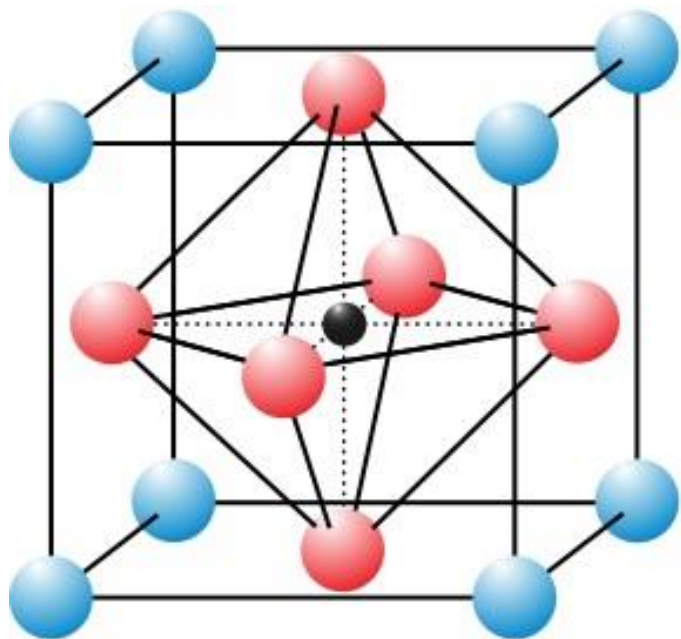
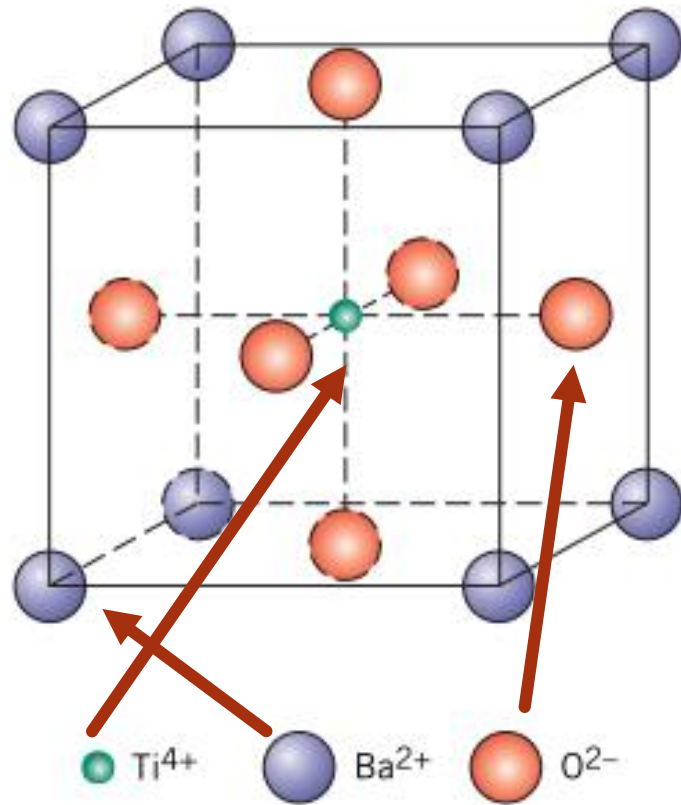
ZnS crystal structure



- Lattice type: FCC lattice.
- Void type: Tetrahedral.
- No. of anion and cations: 4
- Relation a and R : $\frac{1}{4} \times a \sqrt{3} = R_a + R_c$
- Motif: Anions (A): 0 0 0, Cations (B): $\frac{1}{4} \frac{1}{4} \frac{1}{4}$
- 50% occupancy of sites according to the stoichiometry.
- Examples ZnO, ZnS, BeO, SiC, ZnTe etc.



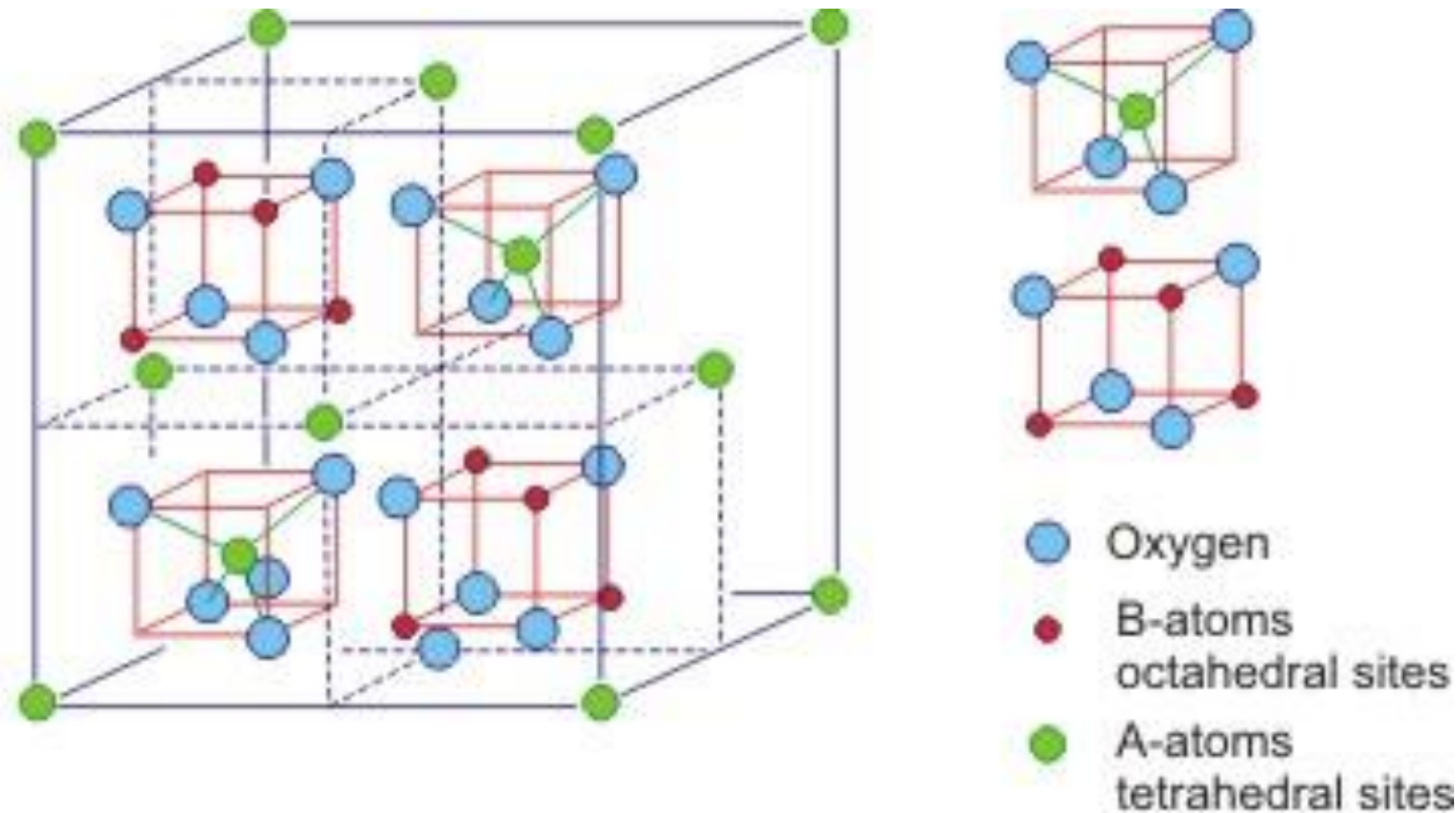
- These are not BCC or FCC structures. These are formed by main lattice from anions and cations being at the void position.



- Lattice type: **Primitive Cubic** (NOT FCC!)
- Motif: A ion - 0 0 0, B ion - $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, O ion - $\frac{1}{2} \frac{1}{2} 0$, $0 \frac{1}{2} \frac{1}{2}$, $\frac{1}{2} 0 \frac{1}{2}$
- Oxygen atoms form an **FCC-like** (not FCC) cell with atoms missing from the corners which are occupied by A atoms.
- Coordination
 - B cation is surrounded by oxygen octahedra which share corners.
- e.g. **$\text{A}^{2+}\text{B}^{4+}\text{O}_3$** , BaTiO_3 , PbTiO_3 , CaTiO_3 , SrTiO_3 etc.
- e.g. **$\text{A}^{3+}\text{B}^{3+}\text{O}_3$** , LaAlO_3 , LaGaO_3 , BiFeO_3 etc.

AB_2O_4 type ionic crystal

- A spinel unit-cell is made up of 8 FCC cells made by oxygen
- consisting of 32 oxygen atoms, 8 A atoms and 16 B atoms.



AB_2O_4 spinel The red cubes are also contained in the back half of the unit cell.

- Crystallize with FCC structure.
- Two cations occupy tetrahedral and octahedral sites in an FCC lattice made by O atoms.
- One unit-cell consists of eight formula units of AB_2O_4
- $1/8$ of 64 TV occupied \rightarrow A
- $1/2$ of 32 OV occupied \rightarrow B

Normal Spinel

Chemical formula: (A²⁺)(B³⁺)O₄

MgAl₂O₄, FeAl₂O₄, CoAl₂O₄ and a few ferrites such as ZnFe₂O₄ and CdFe₂O₄.

In this structure, all the A²⁺ ions occupy the tetrahedral sites and all the B³⁺ ions occupy the octahedral sites.

Inverse Spinel

Chemical formula: (A²⁺)(B³⁺)₂O₄ but can be more conveniently written as B(AB)O₄.

Fe₃O₄ (or FeO.Fe₂O₃), NiFe₂O₄, CoFe₂O₄ etc.

In this structure, ½ of the B³⁺ ions occupy the tetrahedral sites and remaining ½ B³⁺ and all A²⁺ ions occupy the octahedral sites.

1. In CsCl and NaCl structures, 100% of the void positions are occupied.
2. In ZnS type of structure, 50% of the void positions are occupied to maintain stoichiometry.
3. The spinel structure is made by 8 FCC lattices.