Ionic Solids

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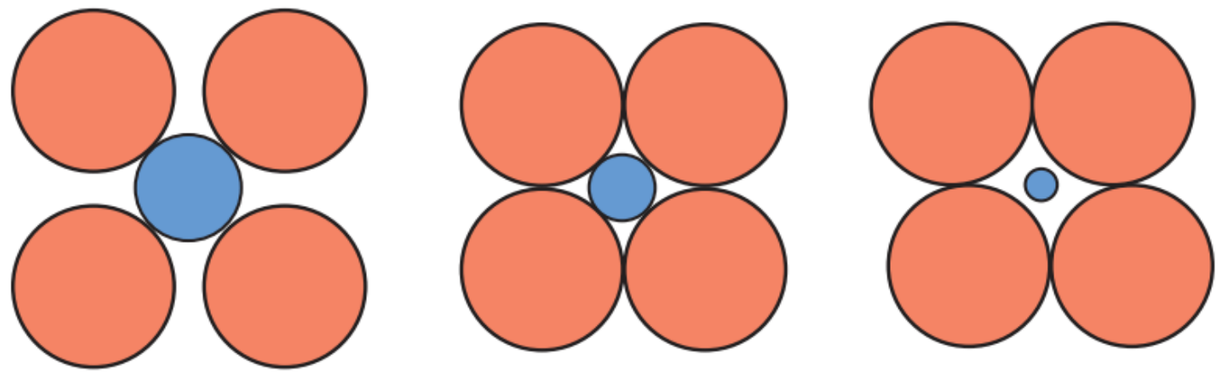
Ionic Solids

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

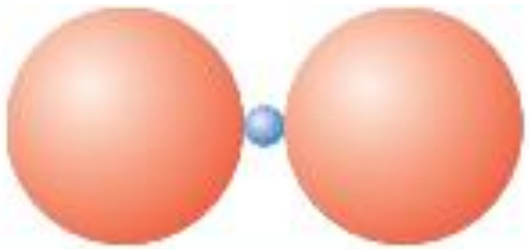
Rules for stable configuration

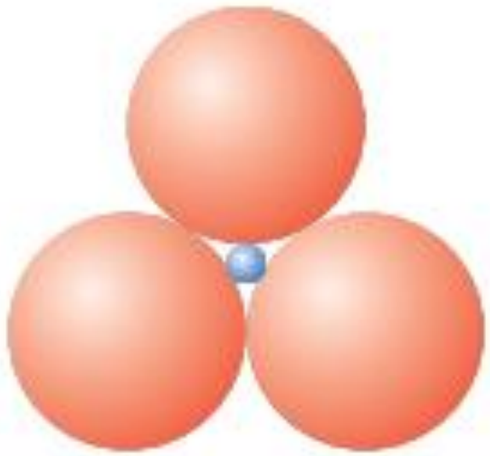
- **No Rattling** → *The cation should not be smaller than the void formed by the anions*
- **Cation size larger than the void** → *The cation should be larger than the void so that the anions do not touch each other*
- **Choose the largest coordination possible** → *Largest coordination gives the best possible packing*

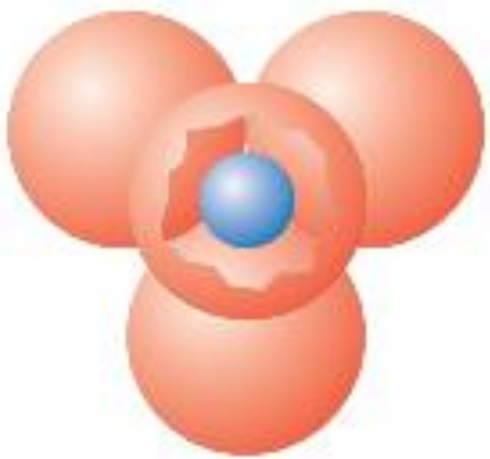


Stable Stable Unstable

Ionic Solids

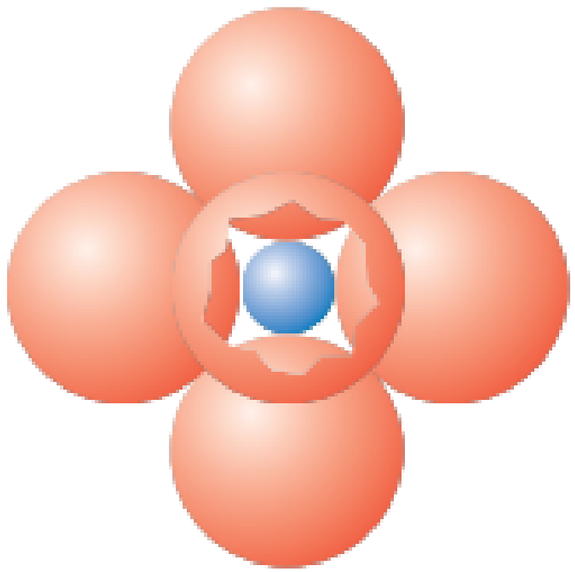


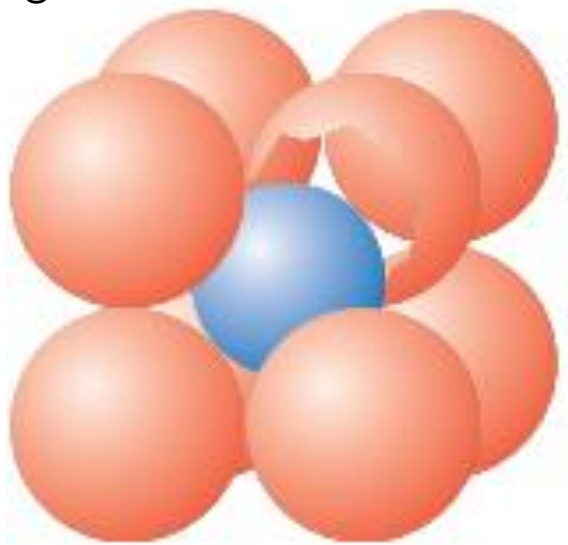




Ligacy	r_c / r_a	Configuration	E.g.	
				r_c / r_a
2	0 – 0.155	Linear		
3	0.155 – 0.225	Triangular		
4	0.225 – 0.414	Tetrahedral		
6	0.414 – 0.732	Octahedral	NaCl	0.54
8	0.732 – 1.0	Cubic	CsCl	0.91
12	1.0	*FCC* or *HCP*		

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





Proof for Rc/Ra ratio

Types of Ionic Crystal

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

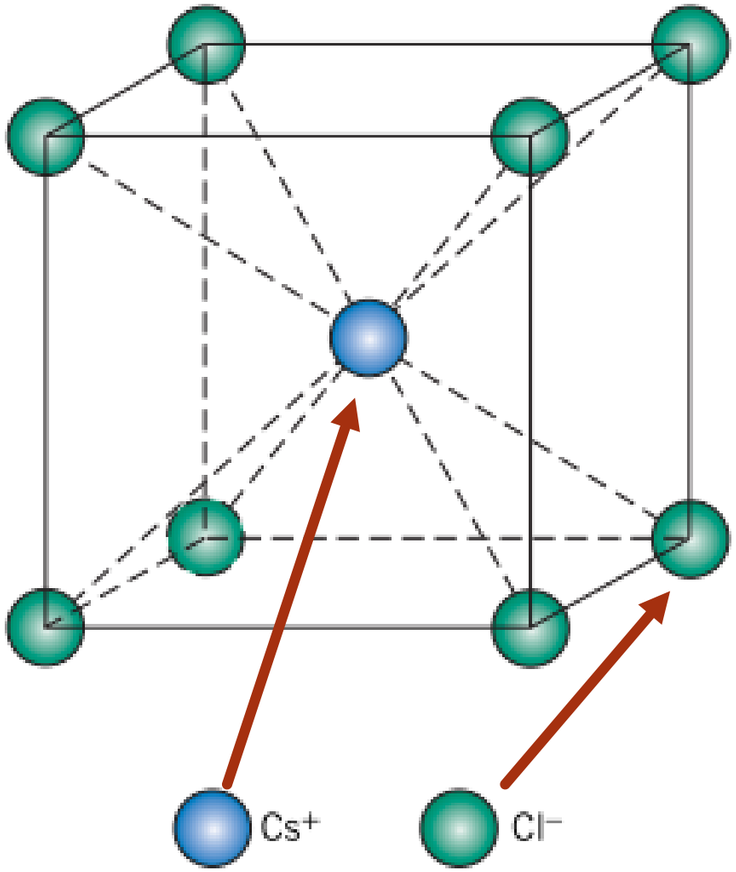
A - cation, B - anion

2. ABO_3 type - Perovskite structure
3. AB_2O_4 type - Spinel structure

A/B – cation, O-oxygen ion (anion)

AX or AB type Ionic crystals

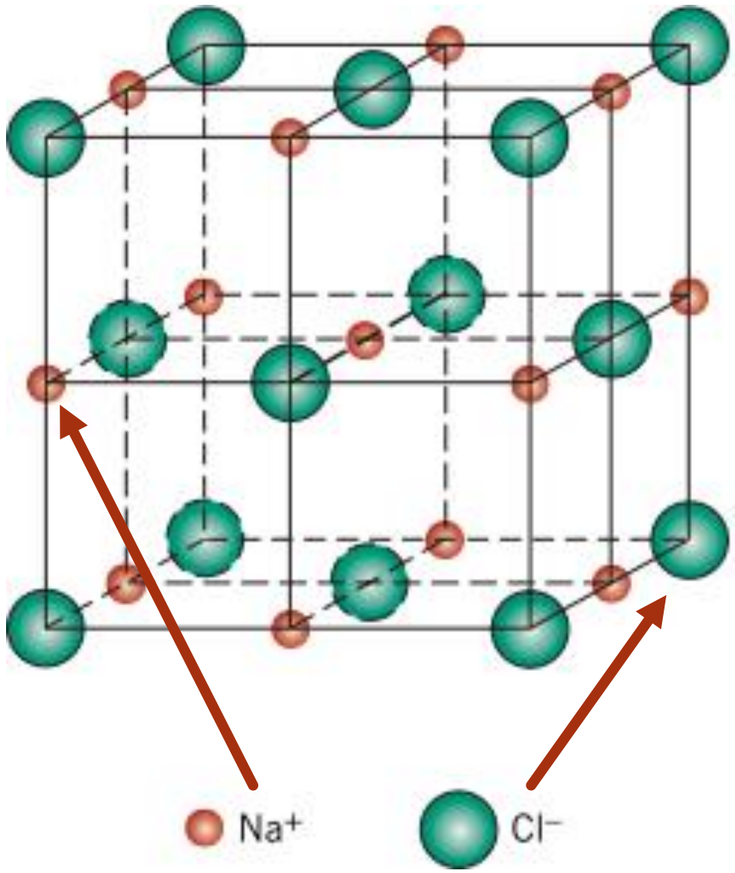
CsCl crystal structure



- Lattice type: Primitive cubic lattice.
- Void type: Cubic type
- No. of anion and cations: 1
- Relation a and R: $a\sqrt{3} = 2\,Ra + 2\,Rc$
- Motif: Anions (A): 0 0 0, Cations (B): ½ ½ ½
- 100% occupancy of sites according to the stoichiometry.
- Examples: Halides such as CSCl, AgI, AgBr, CsI, LiMg etc.

AX or AB type Ionic crystals

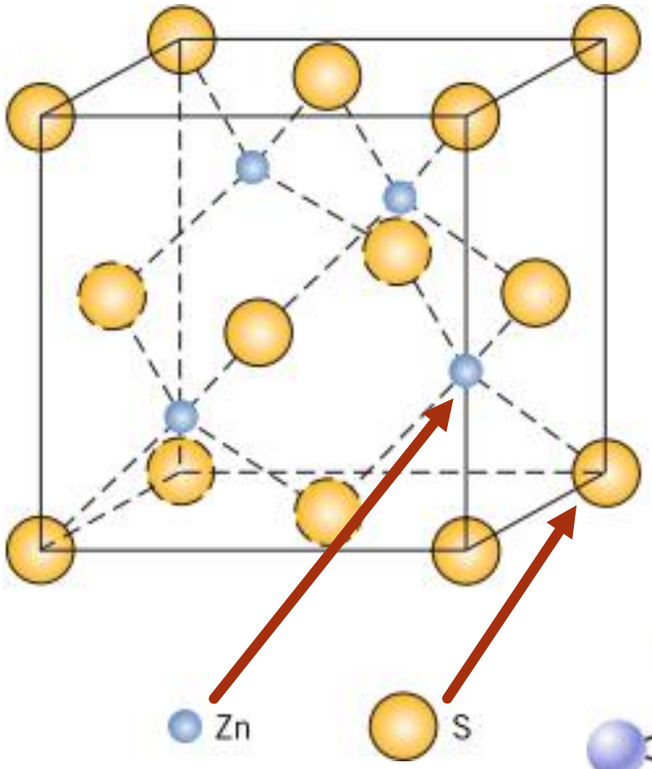
NaCl crystal structure



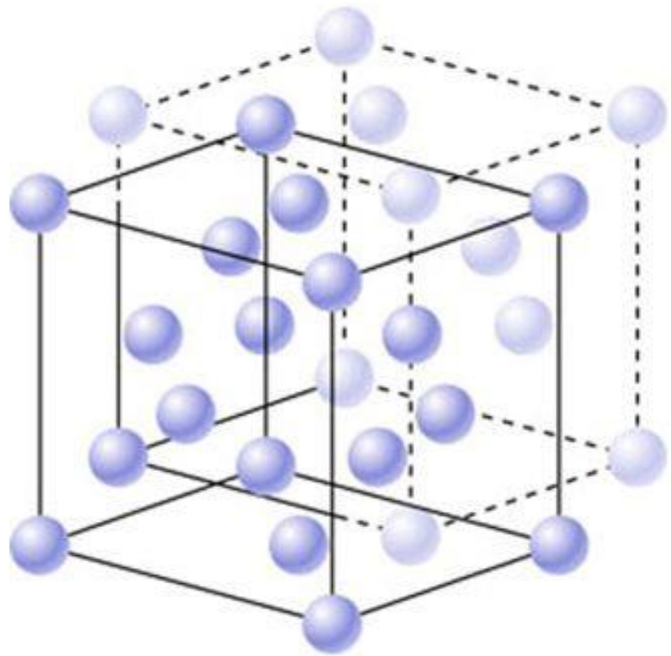
- Lattice type: FCC lattice.
- Void type: Octahedral.
- No. of anion and cations: 4
- Relation a and R: a = 2 Ra + 2 Rc
- Motif: Anions (A): 0 0 0, Cations (B): ½ 0 0
- Anions (A) form the cation sub lattice with FCC structure.
- Cations (B) fill the octahedral sites.
- 100% occupancy of sites according 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



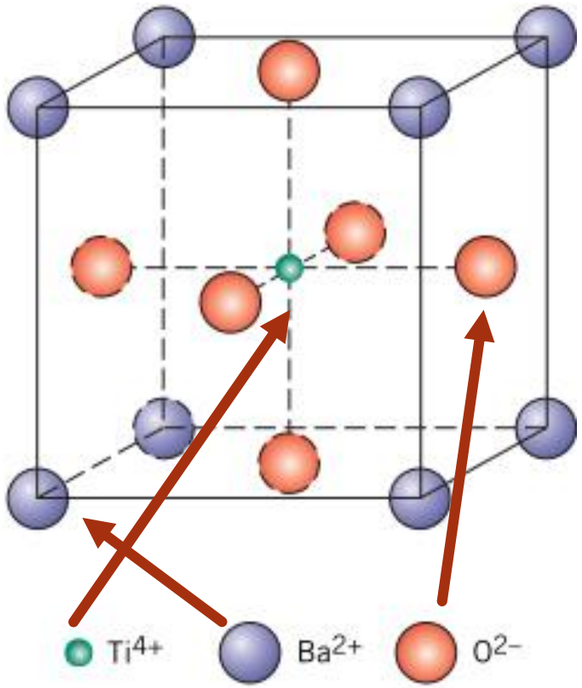
- Lattice type: FCC lattice.
- Void type: Tetrahedral.
- No. of anion and cations: 4
- Relation a and R: ¼ x a √3 = Ra + Rc
- Motif: Anions (A): 0 0 0, Cations (B): ¼ ¼ ¼
- 50% occupancy of sites according to the stoichiometry.
- Examples ZnO, ZnS, BeO, Sic, ZnTe etc.

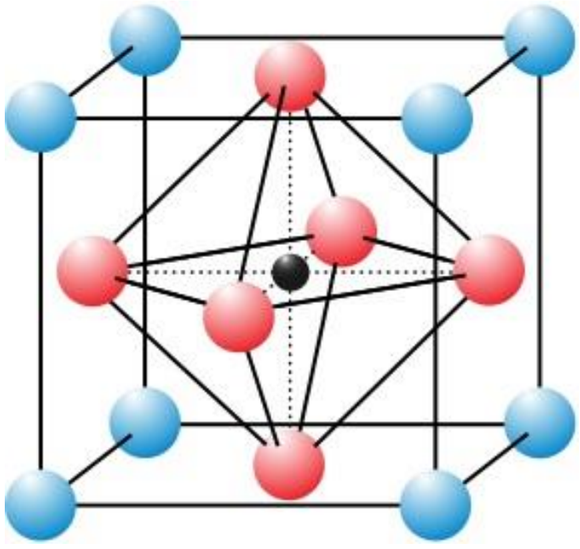


Remember

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

ABO_3 type ionic crystal





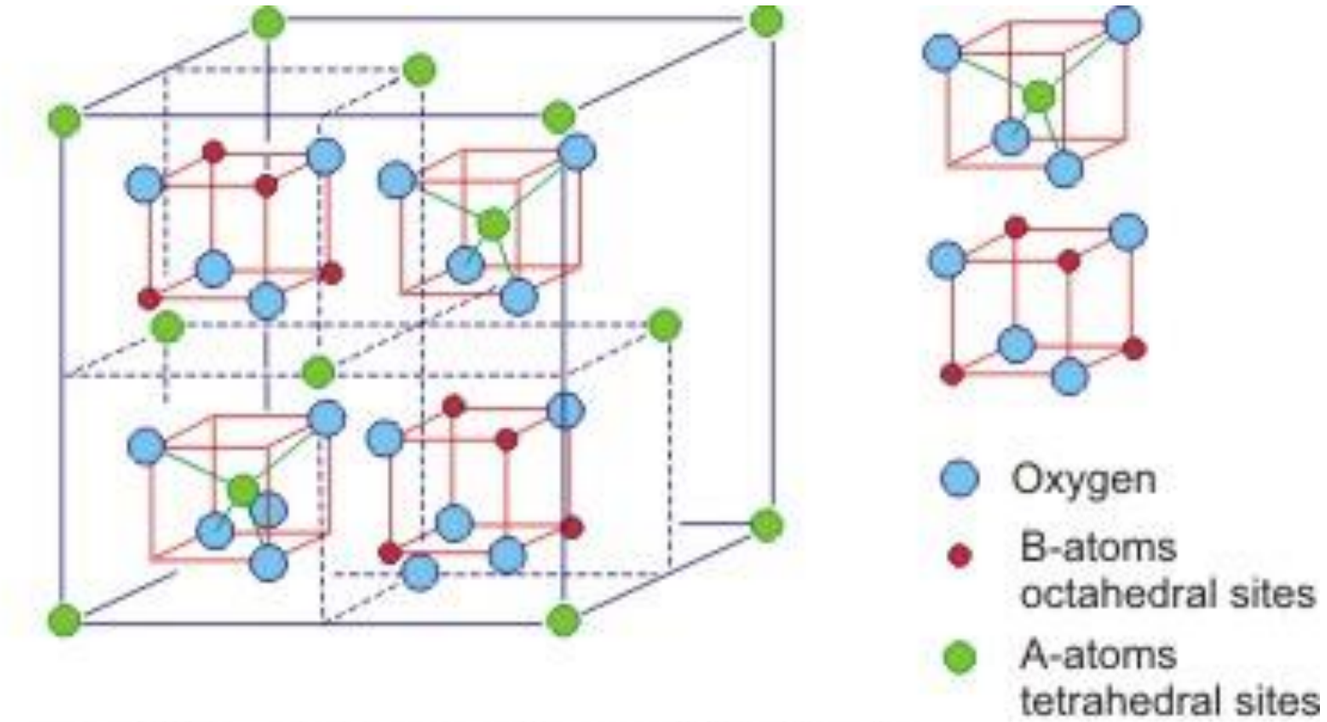
- Lattice type: **Primitive Cubic** (NOT FCC!)
- Motif: A ion - 0 0 0, B ion – ½ ½ ½, O ion - ½ ½ 0, 0 ½ ½, ½ 0 ½
- Oxygen atoms form an **FCC-like** (not FCC) cell with atoms missing from the corners which are occupied by A atoms.

- Coordination
  - B cation is surrounded by oxygen octahedra which share corners.

- e.g. **$A^{2+}B^{4+}O_3$** , $BaTiO_3$, $PbTiO_3$, $CaTiO_3$, $SrTiO_3$ etc.
- e.g. **$A^{3+}B^{3+}O_3$** , $LaAlO_3$, $LaGaO_3$, $BiFeO_3$ 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 → A
- 1/2 of 32 OV occupied → B

AB_2O_4 type ionic crystal

Normal Spinel

Chemical formula: $(A^{2+})(B^{3+})O_4$

$MgAl_2O_4$, $FeAl_2O_4$, $CoAl_2O_4$ and a few ferrites such as $ZnFe_2O_4$ and $CdFe_2O_4$.

In this structure, all the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.

Inverse Spinel

Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as $B(AB)O_4$.

Fe_3O_4 (or $FeO.Fe_2O_3$), $NiFe_2O_4$, $CoFe_2O_4$ etc.

In this structure, ½ of the B^{3+} ions occupy the tetrahedral sites and remaining ½ B^{3+} and all A^{2+}ions occupy the octahedral sites.

Summary

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.