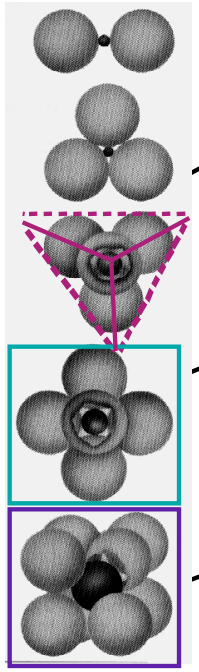
Ceramic crystal structures

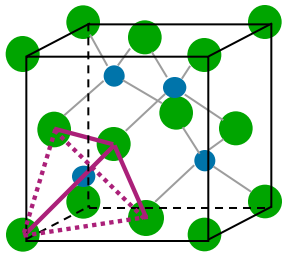
- Need to consider stoichiometry, relative size of ions, bond hybridization

- Coordination # increases with $\frac{r_{cation}}{r_{anion}}$

$\frac{r_{cation}}{r_{anion}}$	Coord #	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	T_D
0.414 - 0.732	6	O_H
0.732 - 1.0	8	cubic

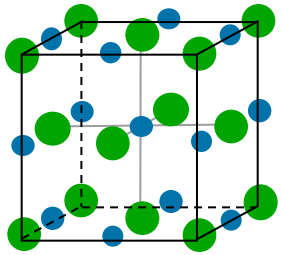
Adapted from Table 12.2, *Callister 7e.*





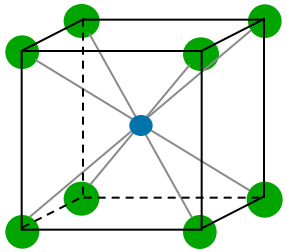
ZnS (zincblende)

Adapted from Fig. 12.4, *Callister 7e.*



NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister 7e.*

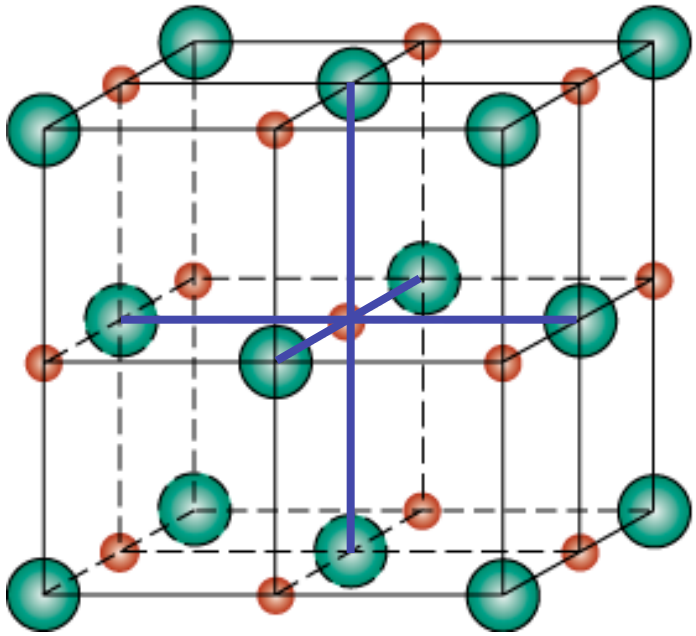


CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister 7e.*

Rock salt structure

Example: NaCl (rock salt) structure



Adapted from Fig. 12.2, *Callister 7e.*

Na^+ r_{Na} = 0.102 nm

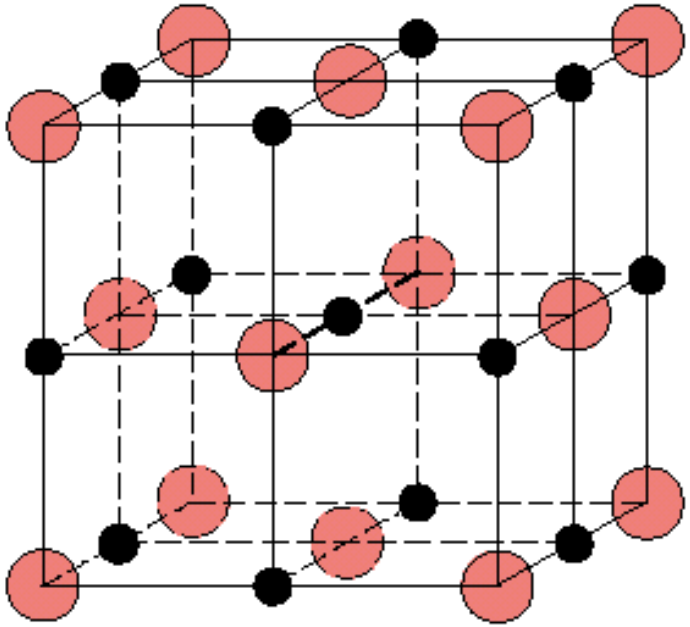
Cl^- r_{Cl} = 0.181 nm

r_{Na}/r_{Cl} = 0.564

$\therefore$ cations prefer O_H sites

MgO and FeO

MgO and FeO also have the NaCl structure



Adapted from Fig. 12.2, *Callister 7e.*

O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

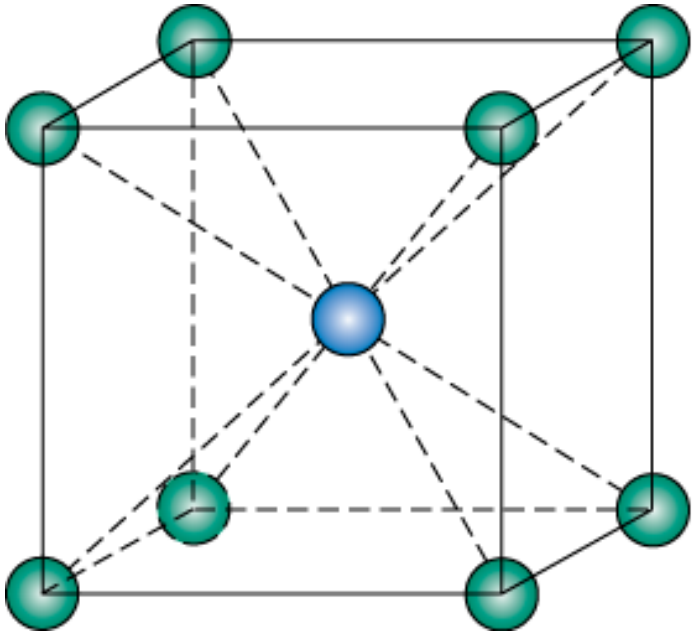
$\therefore$ cations prefer O_H sites

So each oxygen has 6 neighboring Mg^{2+}

AX crystal structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



Cs+

Cl−

$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

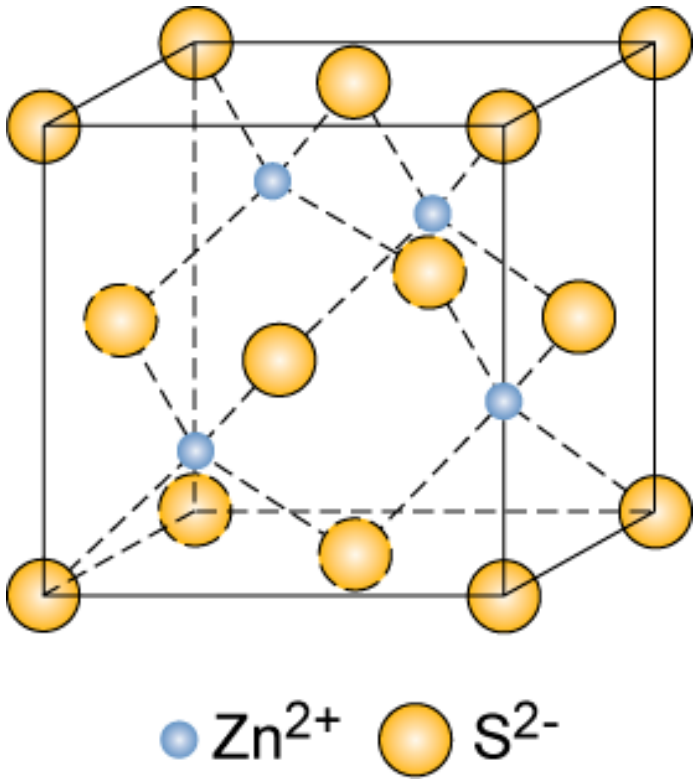
∴ cubic sites preferred

So each Cs^+ has 8 neighboring Cl^-

Adapted from Fig. 12.3, *Callister 7e.*

AX crystal structures

Zinc Blende structure



Adapted from Fig. 12.4, *Callister 7e.*

Ex: ZnO, ZnS, SiC

$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529 \Rightarrow O_H??$$

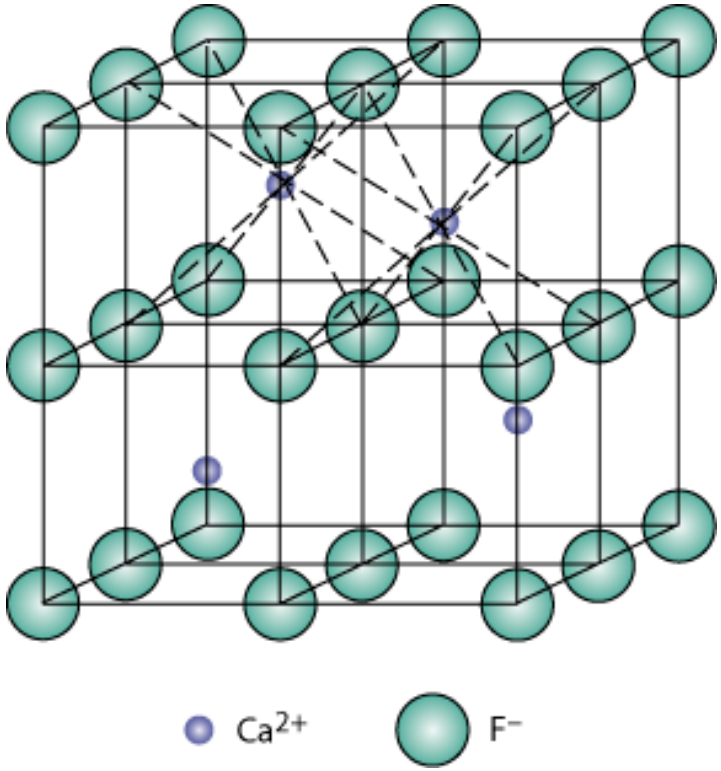
- Size arguments predict Zn^{2+} in O_H sites,
- In observed structure Zn^{2+} in T_D sites

- Why is Zn^{2+} in T_D sites?
  - bonding hybridization of zinc favors T_D sites

So each Zn^{2+} has 4 neighboring O^{2-}

AX_2 crystal structures

Fluorite structure



Adapted from Fig. 12.5, *Callister 7e.*

- Calcium Fluorite (CaF_2)
- cations in cubic sites

- UO_2, ThO_2, ZrO_2, CeO_2

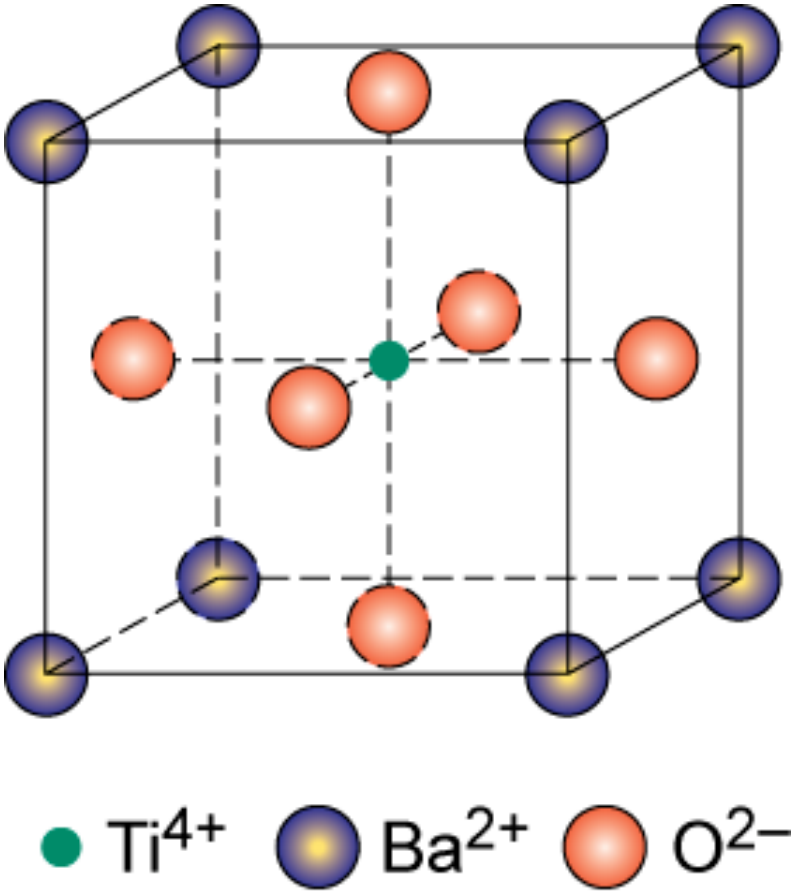
- antifluorite structure – cations and anions reversed

ABX_3 crystal structures

- Perovskite

Ex: complex oxide

$BaTiO_3$



Adapted from Fig. 12.6, *Callister 7e.*