Chapter 9 Structural chemistry of ionic compounds

9.1 Ionic radius ratio & coordination polyhedra of ions

In ***ionic crystals*** the positions in the crystal lattice are occupied by cations and anions.

- In most cases, anions have much larger radii than cations, and form a close-packed structure.

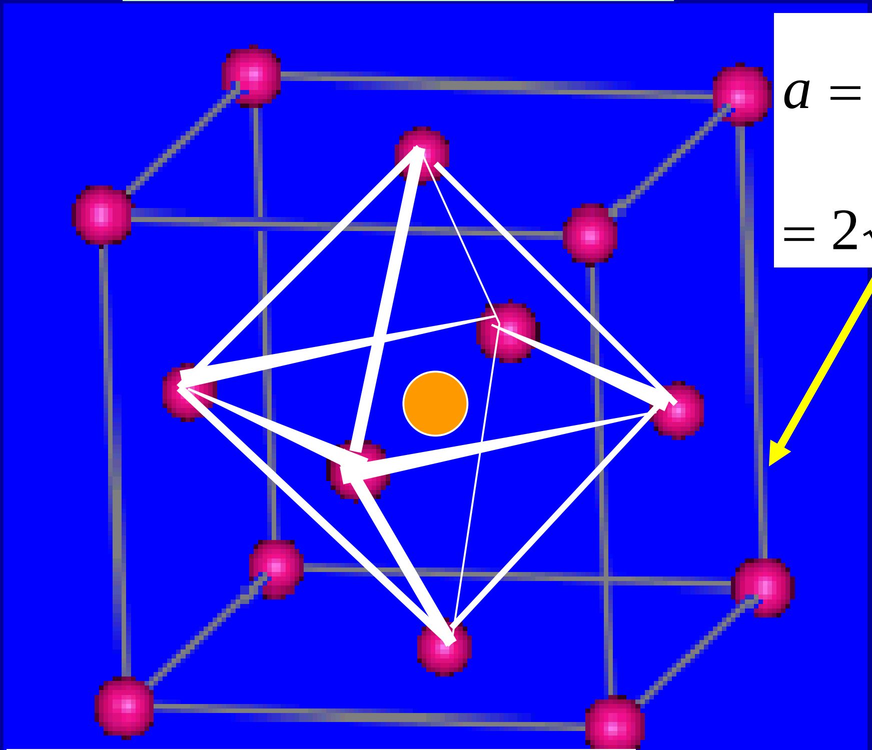
- Consequently cations occupy the interstices of the close-packed structure formed by anions.

➔ Local motif around a cation: coordination polyhedron formed by cation and its surrounding anions.

Interstices in fcc close-packed structure

(If formed by anions with a radius of *R*)

octahedral holes

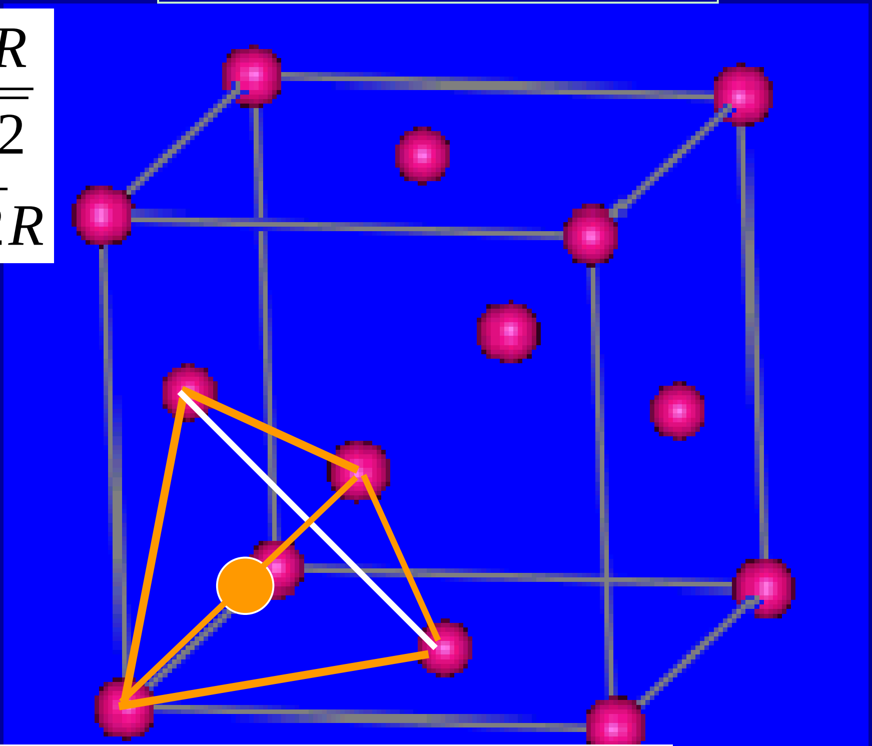


$$a = \frac{4R}{\sqrt{2}} = 2\sqrt{2}R$$

$$R(hole) = \frac{a}{2} - R = 0.414R$$

- **Hole size is 0.414R; CN = 6**

tetrahedral holes



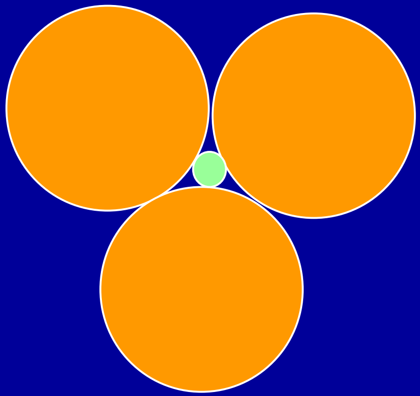
$$R(hole) = \frac{\sqrt{3}a}{4} - R = 0.225R$$

- **Hole size is 0.225R; CN=4**

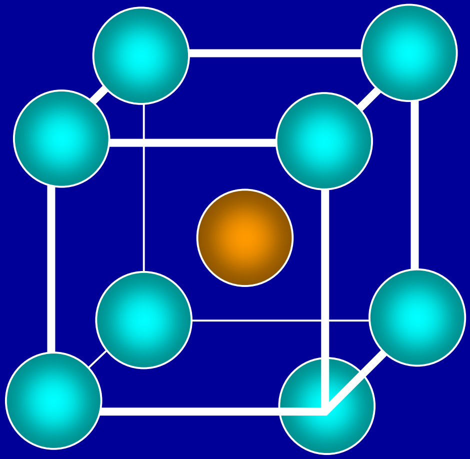
Interstice type	C.N.	r_{hole} /R
Triangular	3	0.155
Tetrahedral	4	0.225
Octahedral	6	0.414
Cubic	8	0.732
Cuboctahedral	12	1.000

Radius of anion

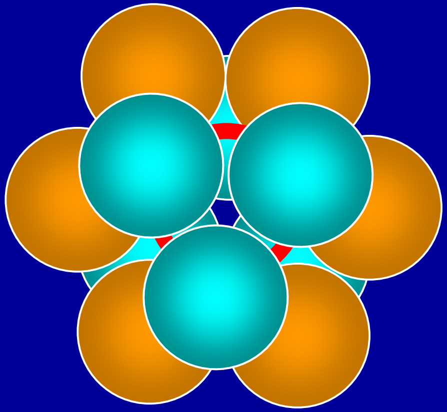
(r_{hole}: the radius of interstice formed by close-packing of anions)



triangular

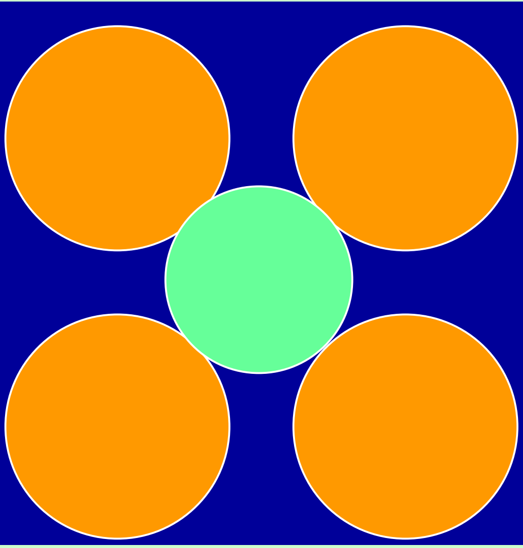


Cubic



Cuboctahedral

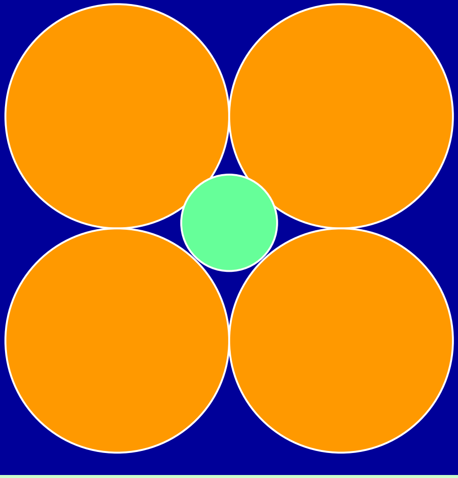
The rule for the packing of ions



Anions directly contact with cation without anion-anion contact.

($R_+ > r_{hole}$)

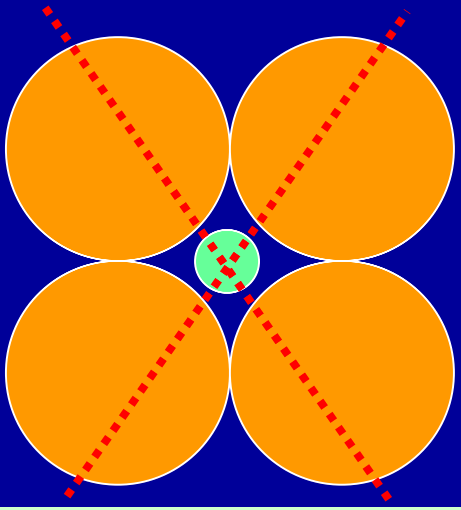
Strong C-A attraction!
Weak A-A repulsion!



Anions directly contact with each other as well as the central cation!

($R_+ = r_{hole}$)

Strong C-A attraction!
Strong A-A repulsion!



Anions directly contact with each other with no cation-anion contact.

($R_+ < r_{hole}$)

weak C-A attraction!
Strong A-A repulsion!

➔ Condition of coordination polyhedron: $R_+ \geq r_{hole}$

Table 1. The limiting R_+/R_- ratio of some coordination polyhedra

Coordination polyhedron	C.N.	minimum R_+/R_-
Triangular	3	≥ 0.155
Tetrahedral	4	≥ 0.225
Octahedral	6	≥ 0.414
Cubic	8	≥ 0.732
Cuboctahedral	12	≥ 1.000

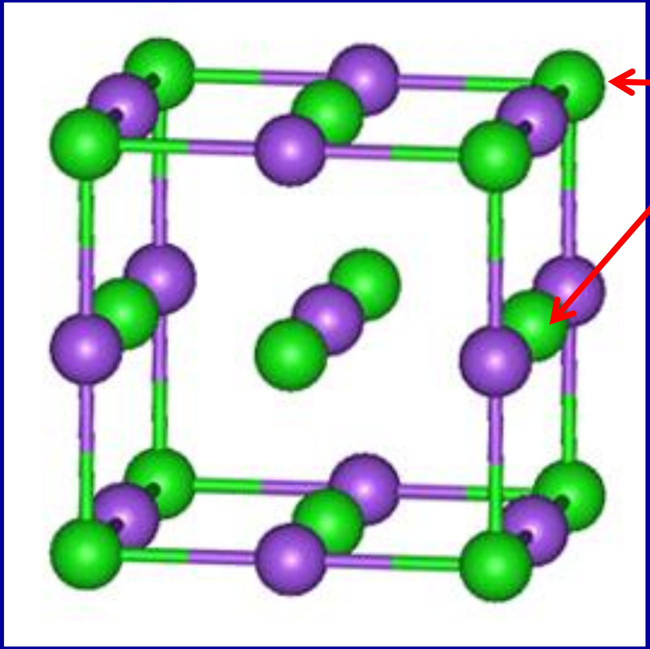
9.2 The crystal structures of some typical ionic compounds

Answer the following questions:

- The packing style of anions ?
- The position of cations ?
- Crystal System (or more precisely ***Bravais Lattice***) ?
- The CN's of anions and cations ?
- Number of atoms in a unit cell ?
- Structural formula ?
- Fractional coordinates of anions/cations

9.2.1 Binary ionic compounds (AB)

Rocksalt structure， NaCl type R_+/R_- ~ 0.732-0.414

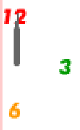


- Packing of anions: fcc/ccp
- Position of cations: Octahedral holes
- Bravais Lattice: Cubic F
- C.N. of A^- & B^+: 6:6
- N_A:N_B in a unit cell: 4:4
- Structural motif: NaCl

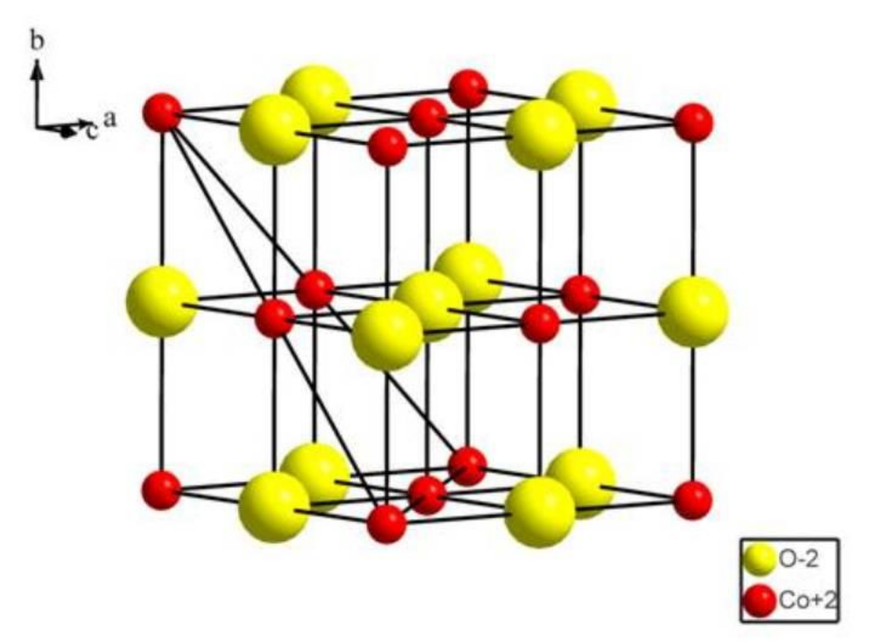
A: 0, 0, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2

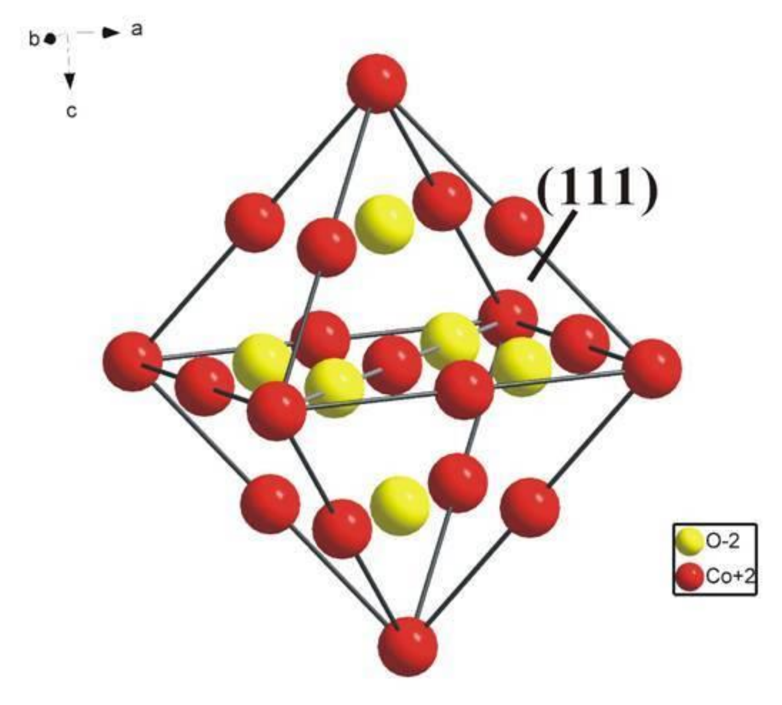
B: 1/2, 1/2, 1/2; 1/2, 0, 0; 0, 1/2, 0; 0, 0, 1/2

(0.732-0.414) KCl, KBr, SrS, RbI, BaTe, SrSe, CaS, KI, SrTe, MgO, LiF, CaSe, NaBr, CaTe, MgS, NaI, LiCl, (>0.732) KF, SrO, BaO, RbF, RbCl, BaS, CuO, CsF, RbBr, BaSe, NaF, (<0.414) MgSe, LiBr, LiF, NiO, CoO …



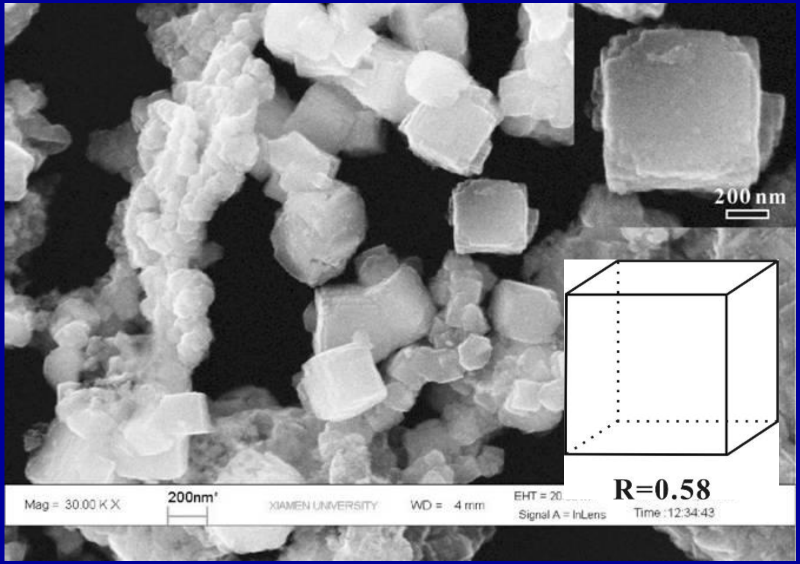
Example 1: CoO



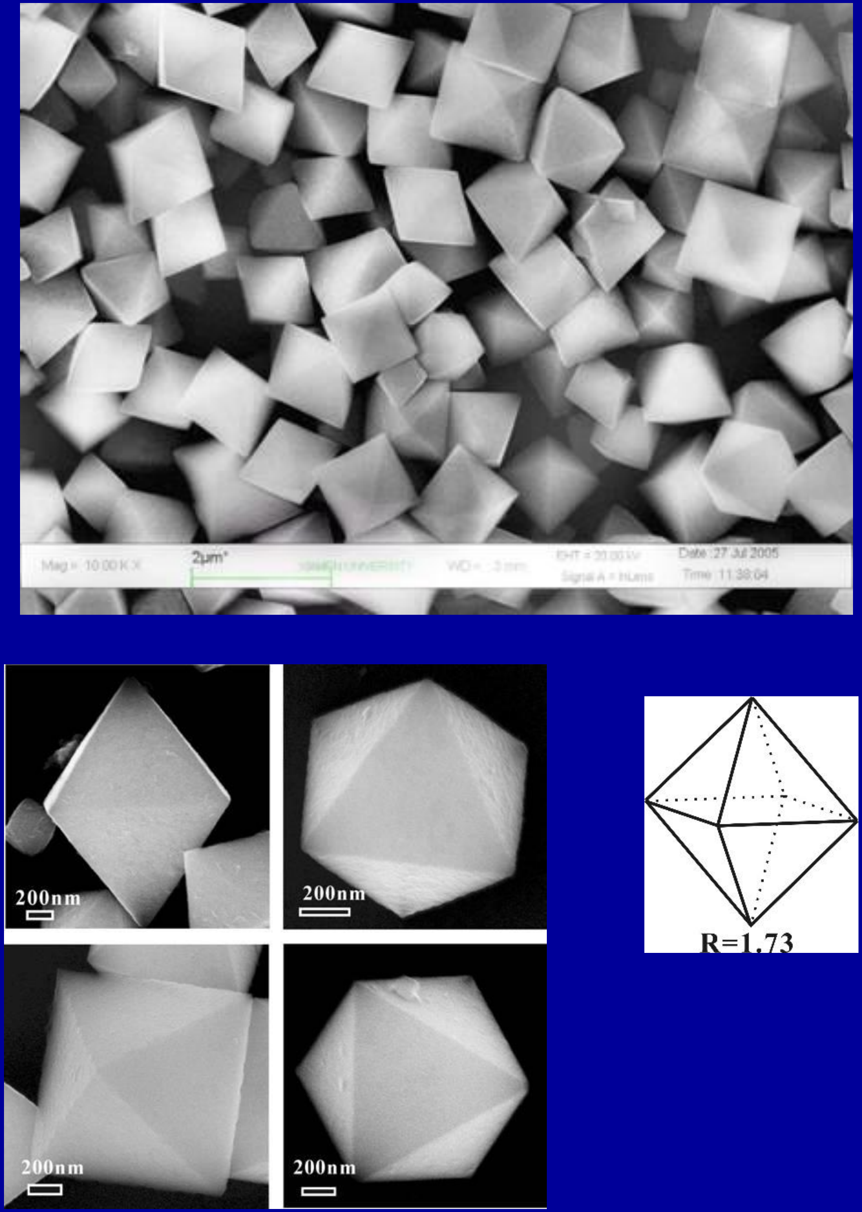


- NaCl-type structure of CoO.
- Its (111) surface are charged, having higher surface energy than other non-polar surfaces.
- However, the charged (111) surface could be stabilized upon coordination of counterions from ionic liquids.

Control the surface by introducing electrostatic interactions!



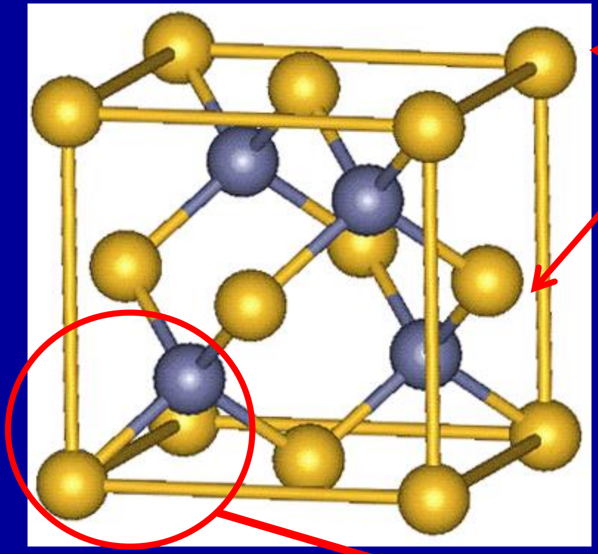
Growth of CoO in the absence of ionic liquid



Growth of CoO in ionic liquid

β-ZnS (Sphalerite/闪锌矿/立方硫化锌)

(R_+/R_-: 0.225-0.414)



- **Packing of anions: fcc/ccp**
- **Position of cations:**

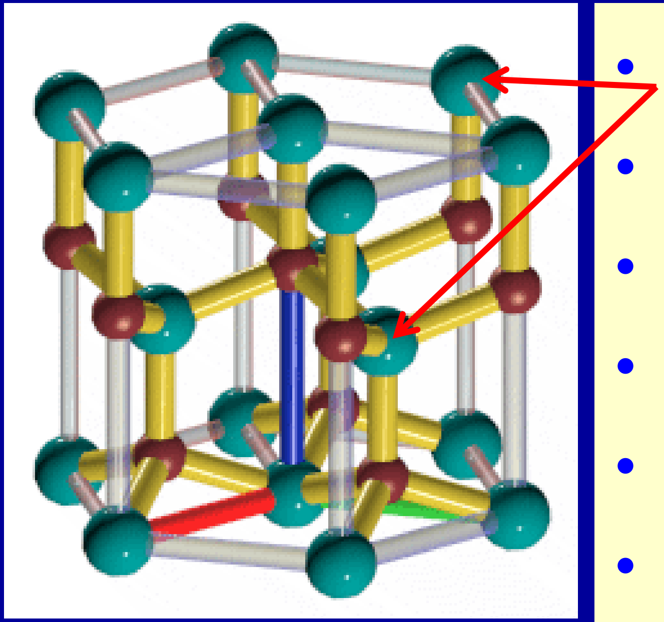
  Tetrahedral holes (1/2)
- **Bravais lattice: cubic F**
- **C.N. of A^- & B^+: 4:4**
- **N_A:N_B in a unit cell: 4:4**
- **Structural motif: ZnS**

A: (0,0,0); (1/2,1/2,0); (1/2,0,1/2); (0,1/2,1/2)

B: (1/4,1/4,1/4); (3/4,3/4,1/4); (3/4,1/4,3/4); (1/4,3/4,3/4)

α-ZnS (R^+/R^- ~ 0.225-0.414)

(Wurtzite/纤锌矿/六方硫化锌)



- **Packing of anions: hcp**
- **Position of cations: Tetrahedral holes (1/2)**
- **Bravais lattice: hexagonal P**
- **C.N. of A^- & B^+: 4:4**
- **N_A:N_B in a unit cell: 2:2**
- **Structural motif: Zn_2S_2**

A: (0,0,0); (1/3, 2/3, 1/2)

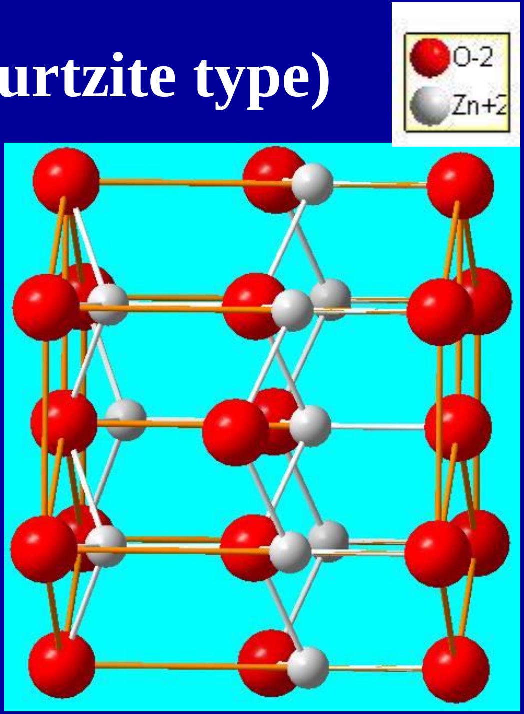
B: (0, 0, 3/8); (1/3, 2/3, 7/8)

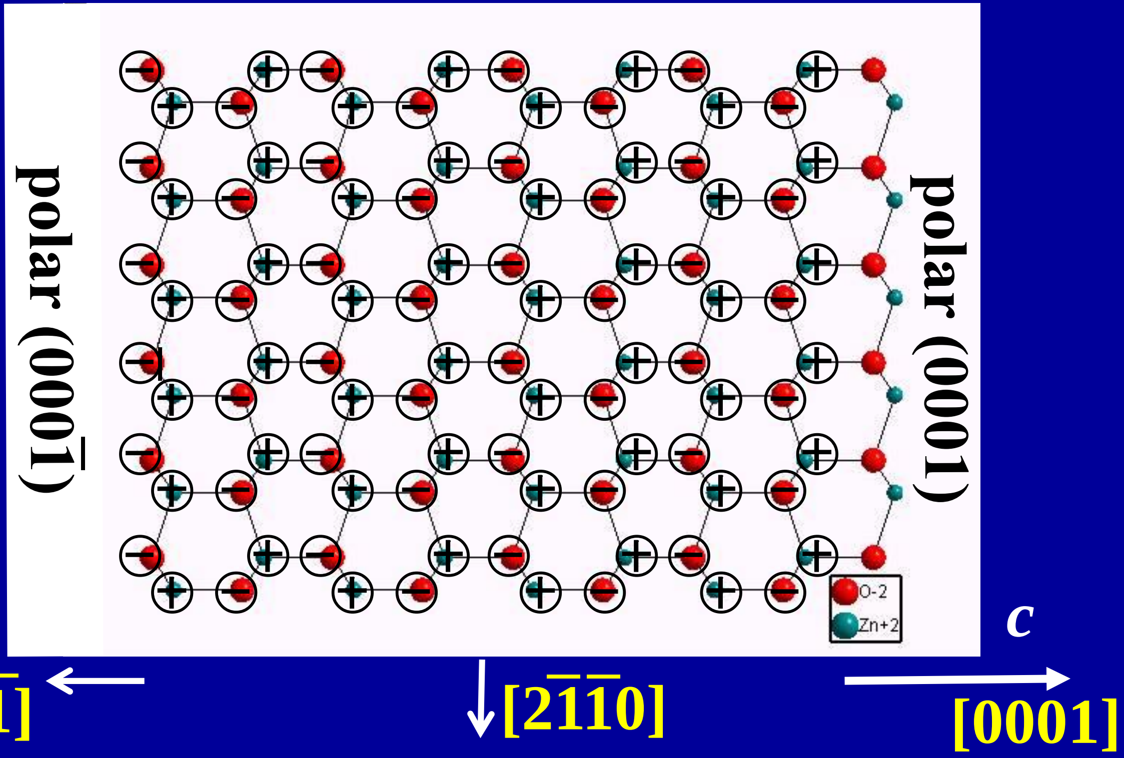
CuF, CuCl, CuBr, CuI; AgI; ZnO, ZnS, ZnSe, ZnTe; CdO, CdS, CdSe, CdTe; HgS, HgSe, HgTe, (CoO, MnO)

Example: ZnO --- Growth of unusual morphologies

Crystal structure of ZnO

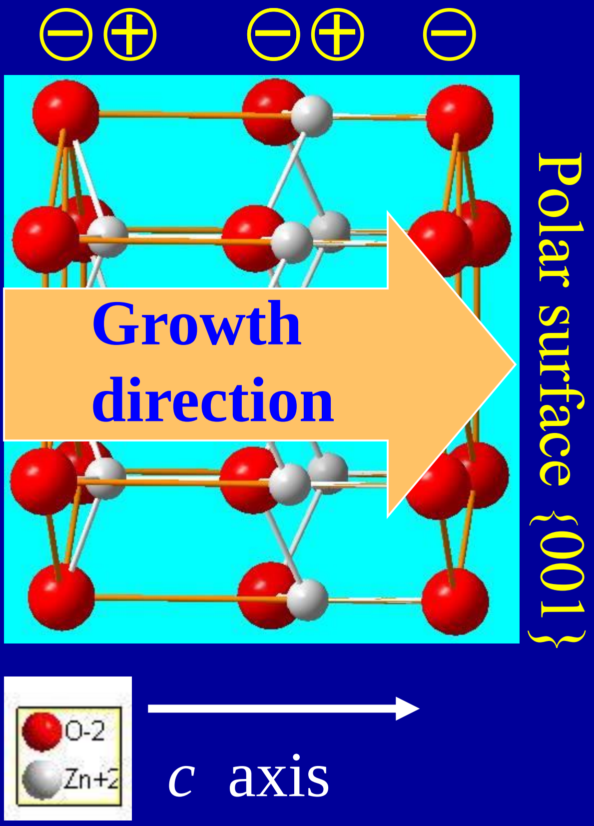
(Wurtzite type)





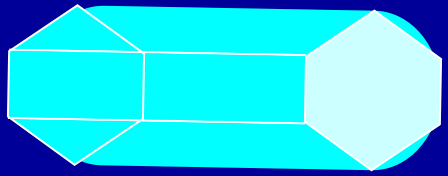
Non-polar surfaces: $(10\bar{1}0)$, $(01\bar{1}0)$, $(1\bar{1}00)$, $(2\bar{1}\bar{1}0)$

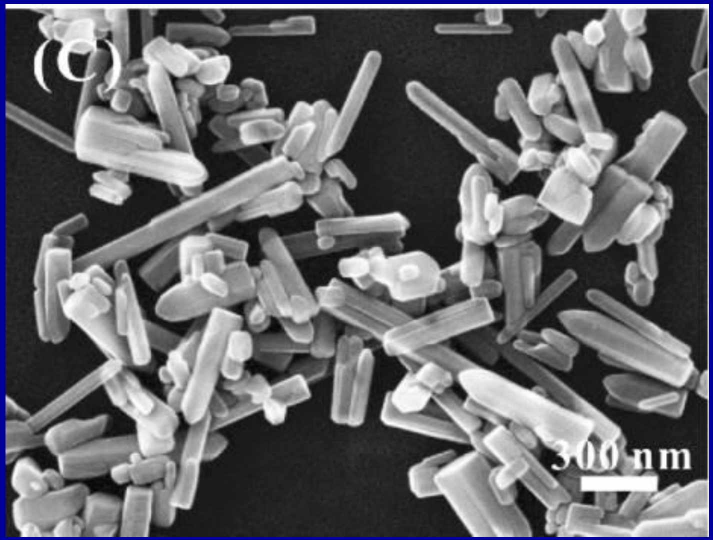
The polar surfaces (0001) and $(000\bar{1})$ have higher surface energies than other non-polar surfaces do!



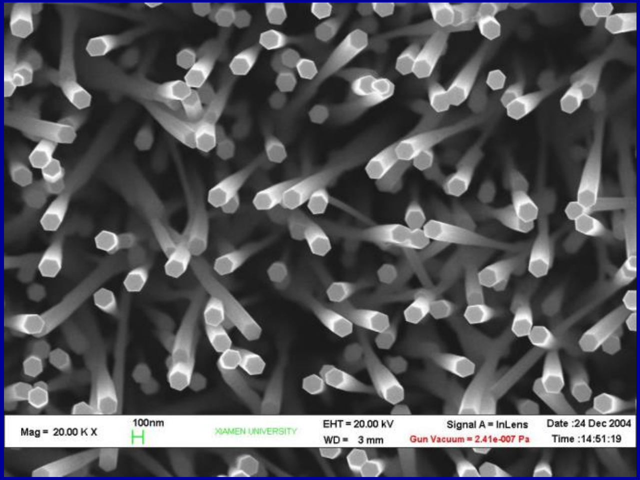
Normal growth

Non-polar {100}

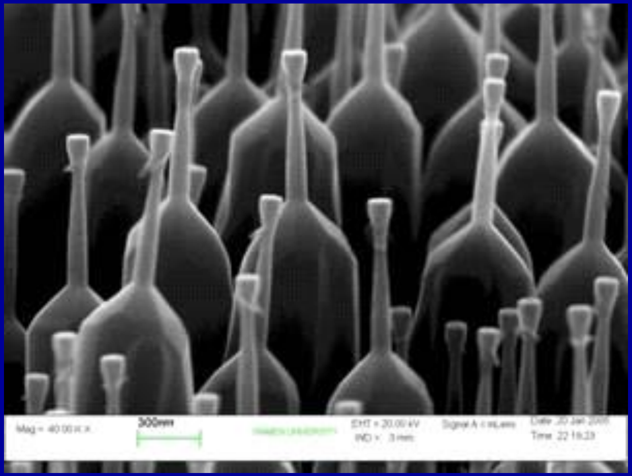




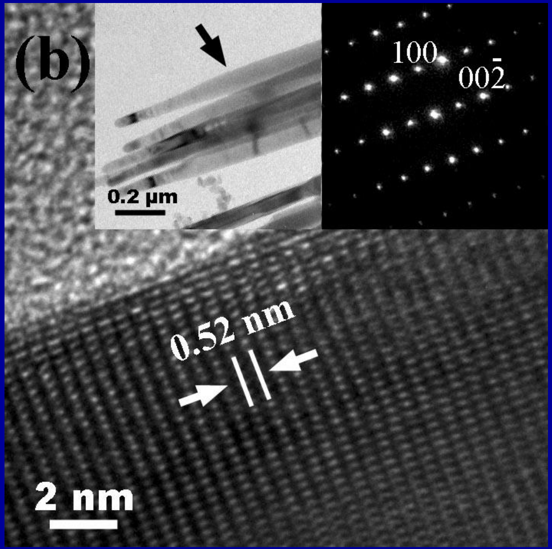
Growing into rod-like morphology along ***c*** axis to give rise to those stable non-polar surfaces exposed.



Thermo CVD of ZnO on Silicon surfaces



Micro-wave plasma CVD of ZnO on Silicon surfaces



thermo-decomposing $Zn(CH_3COO)_2$

ZnO tends to grow into nanowires with [0001] as growth direction.

Control the surface energy by Electrostatic interaction

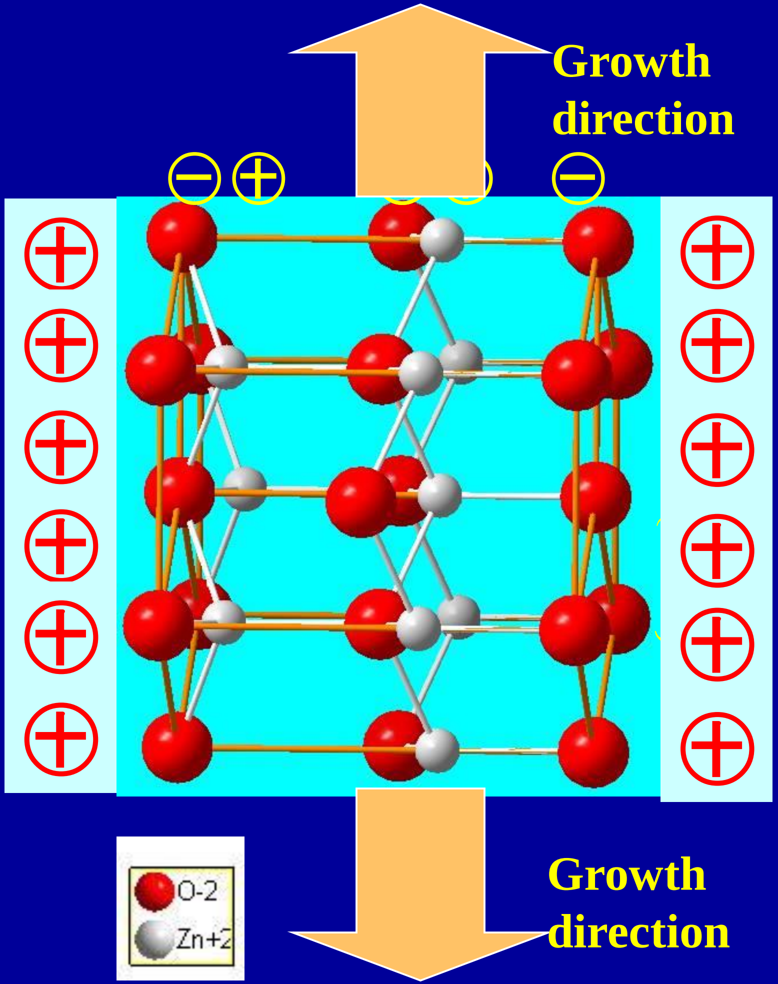
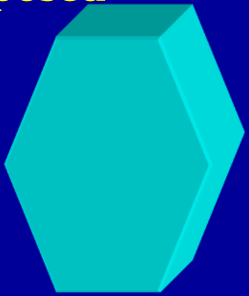
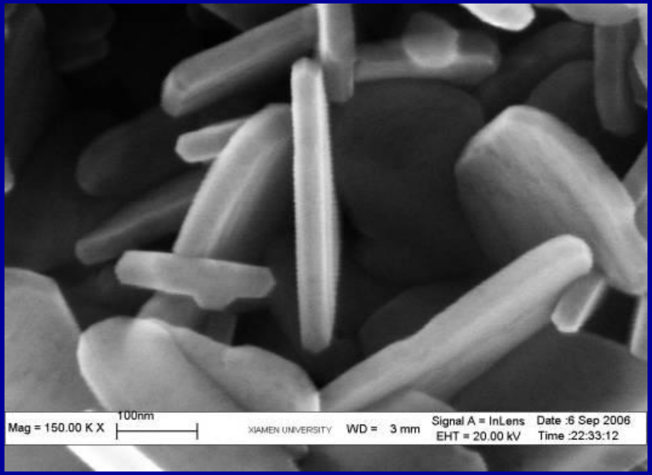


Plate-like with {001} surface exposed

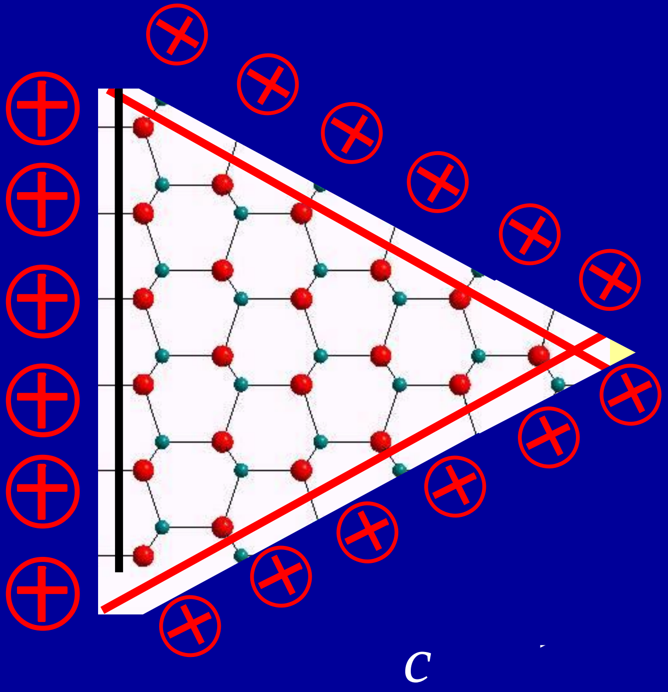


Saturated solution of salt

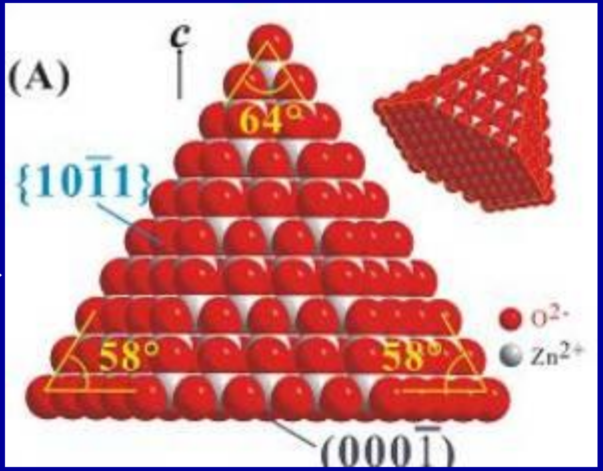


{001} surfaces exposed

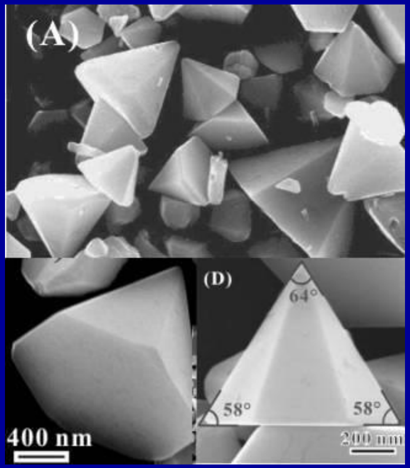
Enhancing the electrostatic interactions



All polar surface exposed



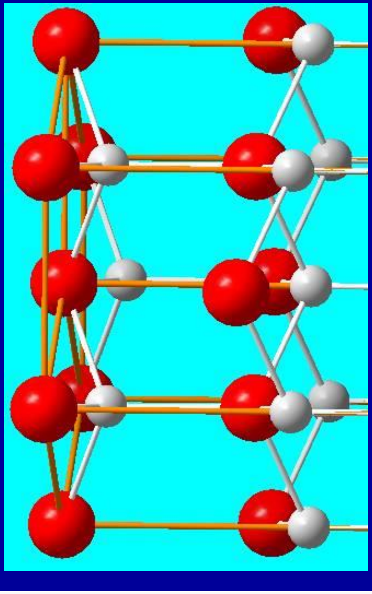
Molten salt



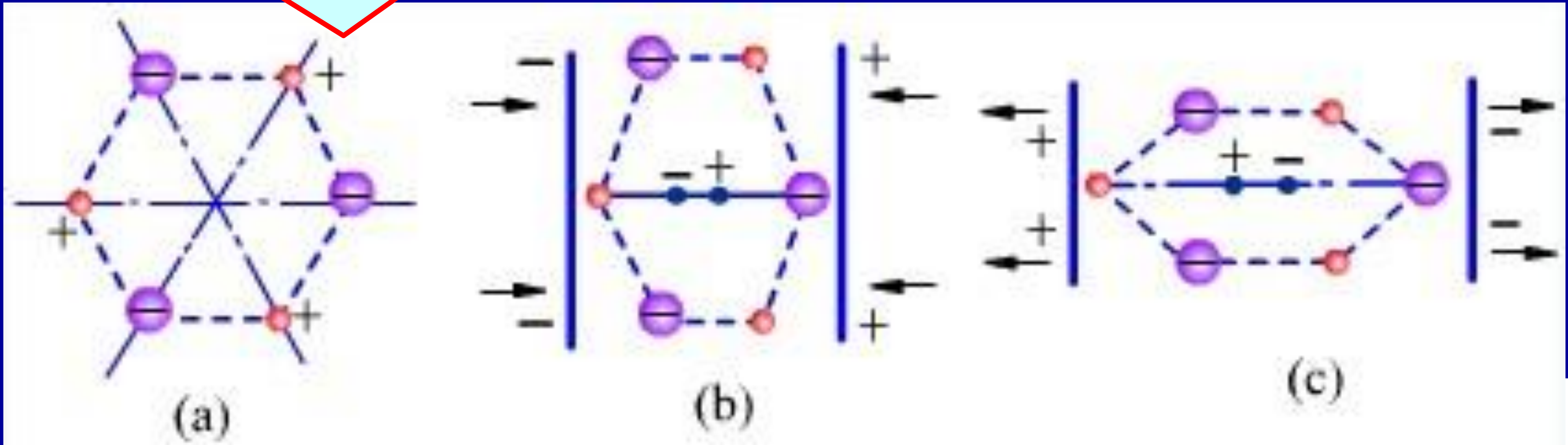
Chem. Comm. 5572 (2005)

Why do we need ZnO with polar surfaces exposed?

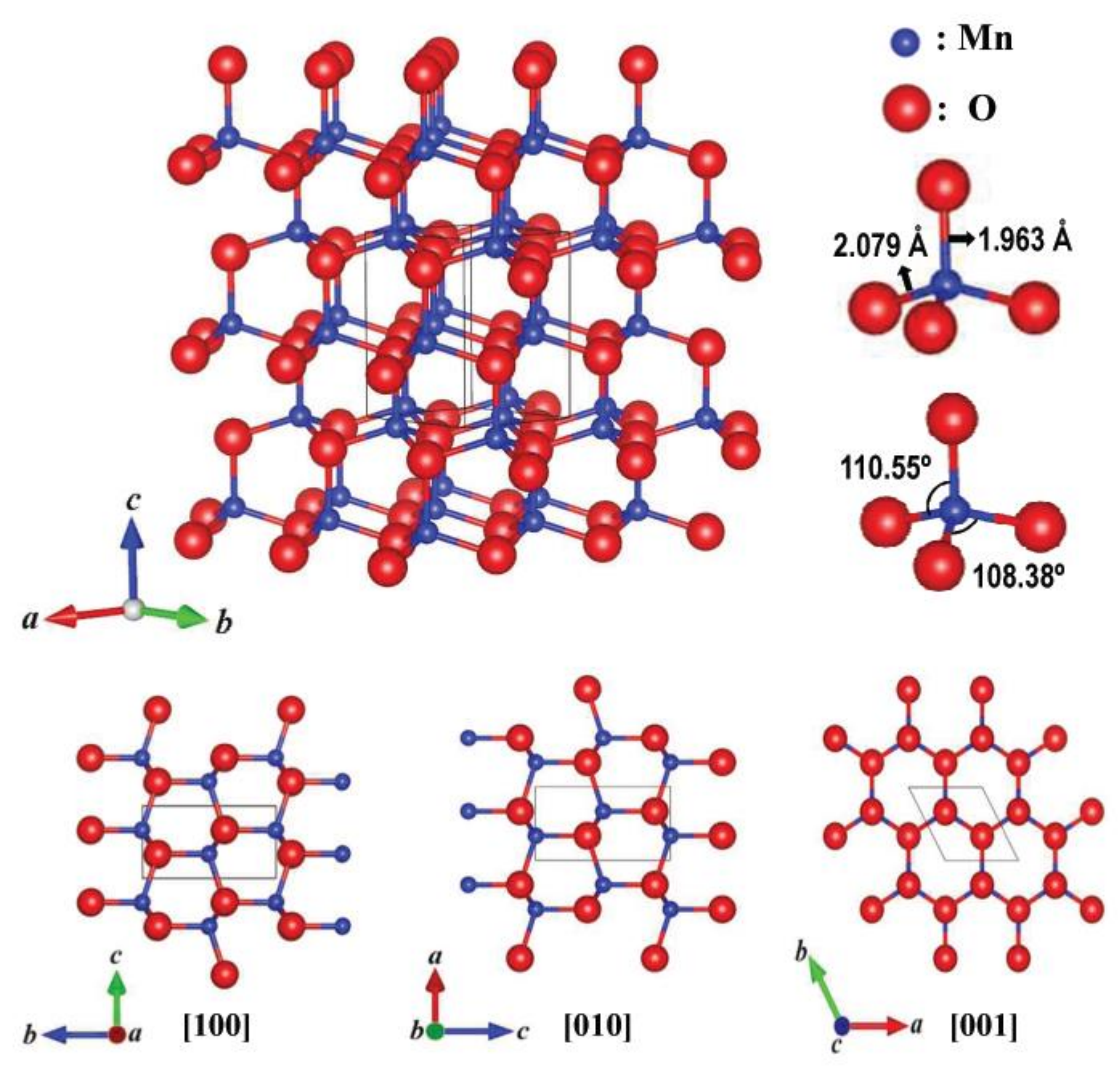
piezoelectric effect



Ionic crystals with polar surfaces exposed always exhibit piezoelectric effect, a physical property that can be exploited to turn mechanical energy into electricity.



Wurzite: New Solid phase of MnO

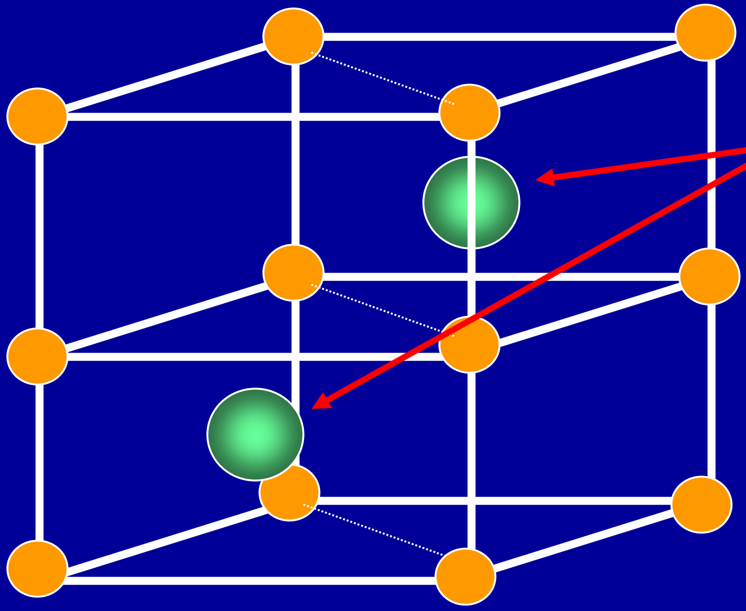


Wurzite structure of MnO

J. Am. Chem. Soc. 2012, 134, 8392

- Most transition metal oxides (MO, M= Sc, ….Ni) have a cubic rocksalt crystal structure.
- But ZnO and CoO are the only stable transition metal oxides known to possess a hexagonal structure.
- Recently, the hexagonal structure of MnO has been synthesized by Park, J. T. et al.

NiAs (R^+/R^-: 0.732-0.414) FeS



Normal picture

- **Packing of anions: hcp**

(Two anions within a primary cell!)

- **Cations: All octahedral holes**
- **Bravais Lattice: hP**
- **C.N. of A^- & B^+: 6:6**
- **N_A:N_B in a unit cell: 2:2**
- **Structural motif: Ni_2As_2**

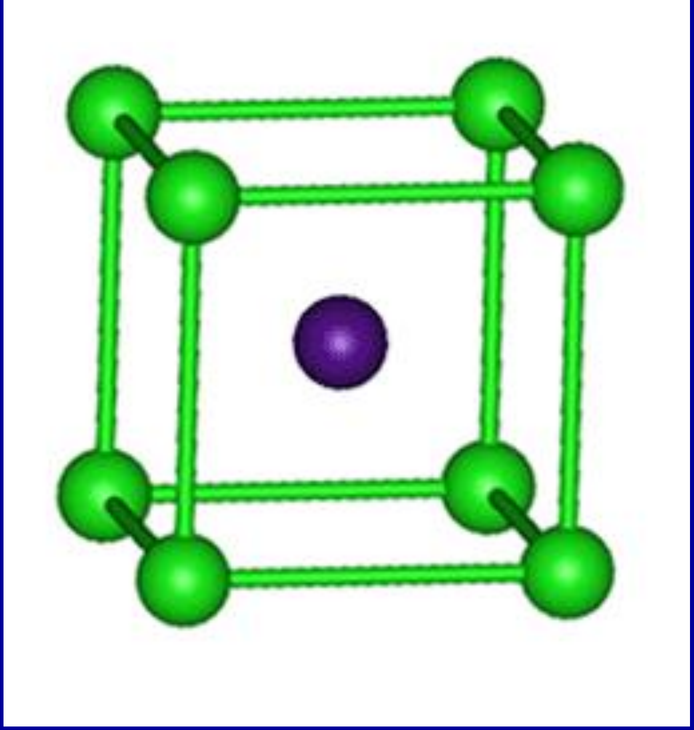
Alternative picture: Cations ~ layered hexagonal structure

Anions： triangular prism holes (1/2)

Ni: 0, 0, 0; 0, 0, 1/2 As: 1/3, 2/3, 1/4; 2/3, 1/3, 3/4;

CsCl cubic, $C.N.^+:C.N.^-$ 8:8

CsBr, CsI (R_+/R_- : 1-0.732)



• The packing of anions:	Cubic
•Bravais Lattice :	Cubic P
•The position of cations:	Cubic holes
The C.N. of cation and anion:	8:8
• Atom number in one unit cell:	1:1

A: 0,0,0

B: 1/2,1/2,1/2

Please think about the coordination-polyhedra representation for this type of crystals! (co-edge or cofacial stack?)

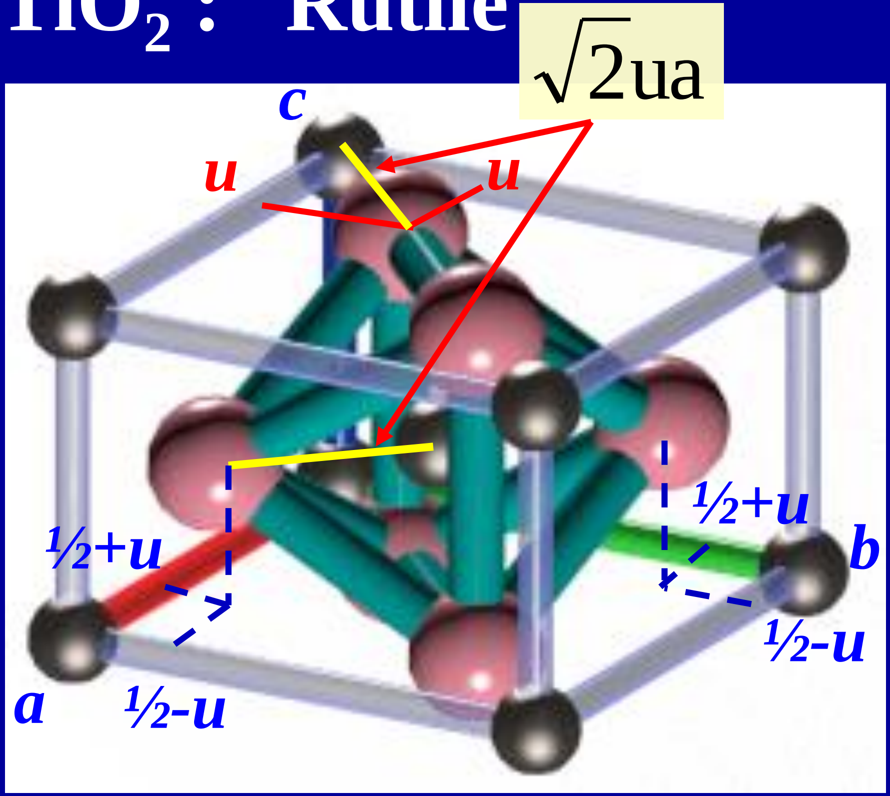
The crystal structures of some typical ionic compounds

AB_2: TiO_2, CaF_2, etc.

Answer the following questions:

- The packing style of anions ?
- The position of cations ?
- Crystal System (Bravais Lattice) ?
- The CN’s of anions and cations ?
- Number of atoms in a unit cell ?
- Structural formula ?
- Fractional coordinates of anions/cations

TiO_2 : Rutile



• The packing of anions:	**Distorted hcp**
•Bravais Lattice :	**Tetragonal P**
•The position of cations:	**1/2 distorted octahedral holes**
The C.N. of cation and anion:	**6:3**
• Atom number in one unit cell:	**Ti:O = 2:4**

A: 0,0,0; 1/2,1/2,1/2 (Ti)

B: u,u,0; -u,-u,0; 1/2+u, 1/2-u, 1/2; 1/2-u, 1/2+u, 1/2. (O) {TiO_2,u=0.31}

(0.732-0.414) TeO_2, MnF_2, PbO_2, FeF_2, CoF_2, ZnF_2, NiF_2, MgF_2, SnO_2, NbO_2, MoO_2, WO_2, OsO_2, IrO_2, RuO_2, TiO_2, VO_2, MnO_2, GeO_2

Rutile TiO_2

Wine-red, adamantine luster

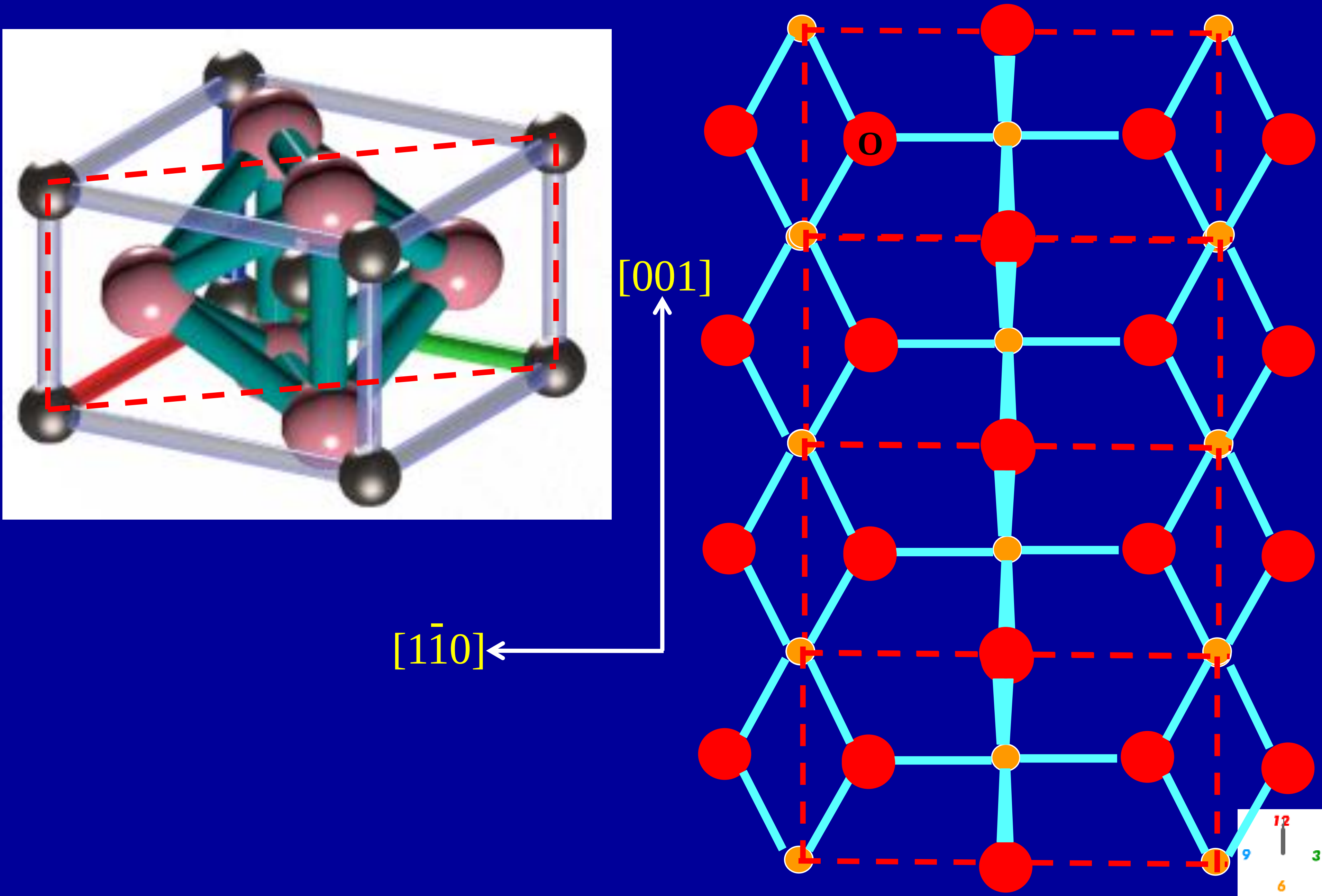
Group space: P 4/mmm

a = 4.5937 Å, c = 2.9587 Å;   Z = 2

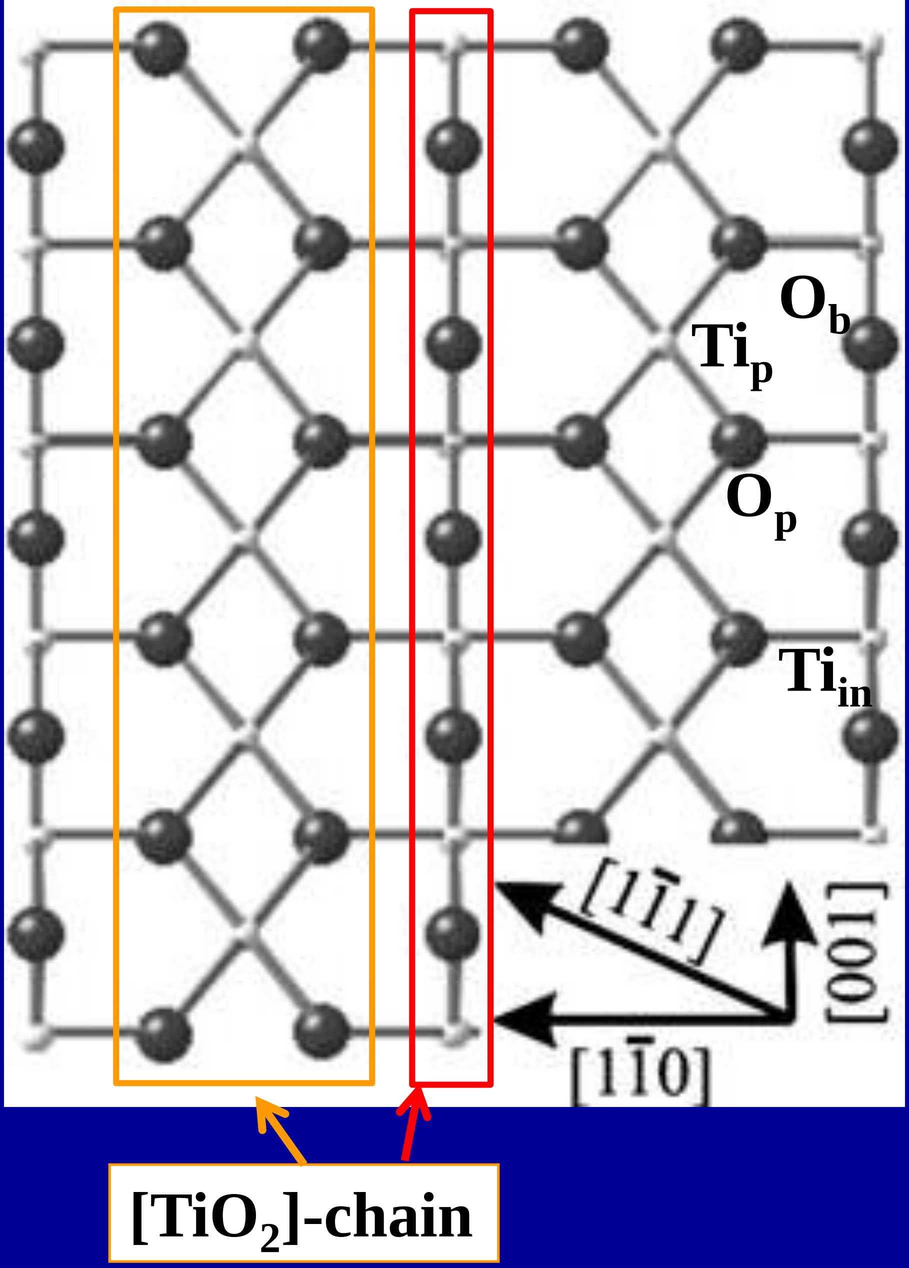
Selected applications:

- Powdered: white pigment!
- Nano-sized: highly effective in absorption of UV-radiation (sunscreens) ……

(110) Surface of Rutile (SnO_2, TiO_2) crystal



(110) Surface of Rutile (SnO_2, TiO_2) crystal



O_b: out-of-plane bridging O

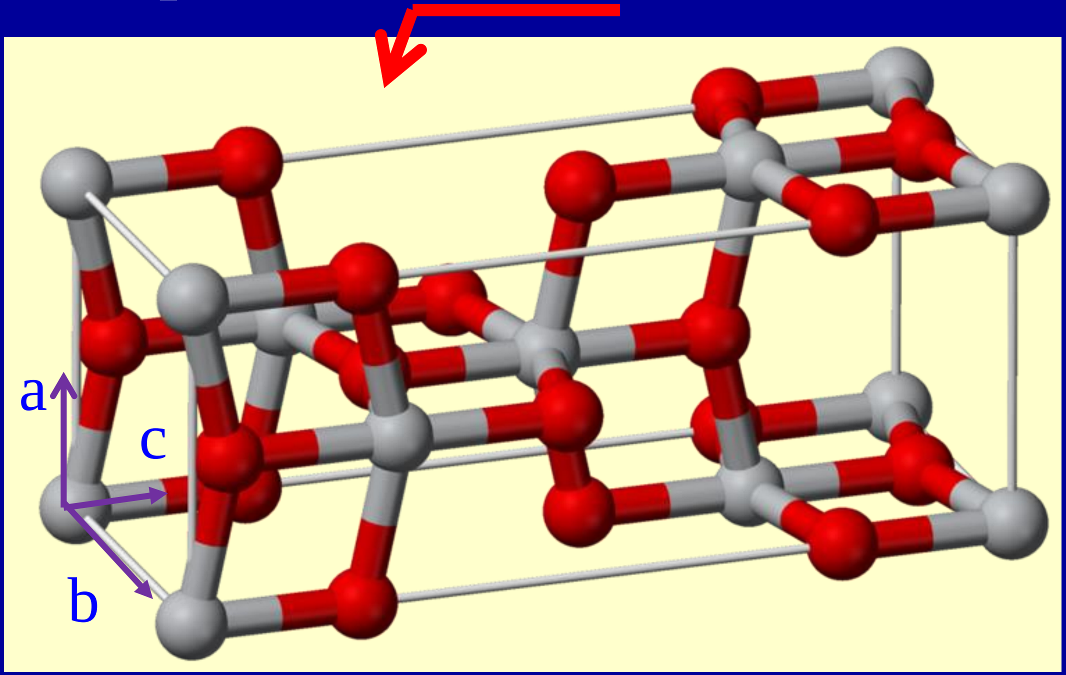
O_p: in-plane O atom

Ti_p: in-plane Ti atom

Ti_{in}: subsurface Ti atom

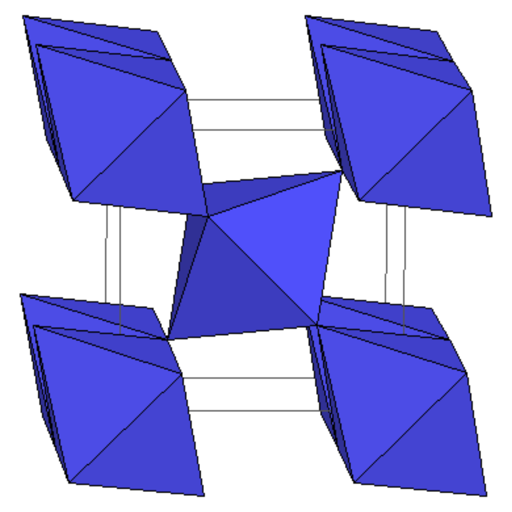
- In TiO_2 crystal, the planes of neighboring [Ti-O_2]-chain are perpendicularly aligned with each bridging O coordinated to a Ti atom of a neighboring chain.
- Thus, each lattice O is 3-coordinate and each lattice Ti being 6-coordinate.
- In the (110) surface, there are two types of O atoms exposed .

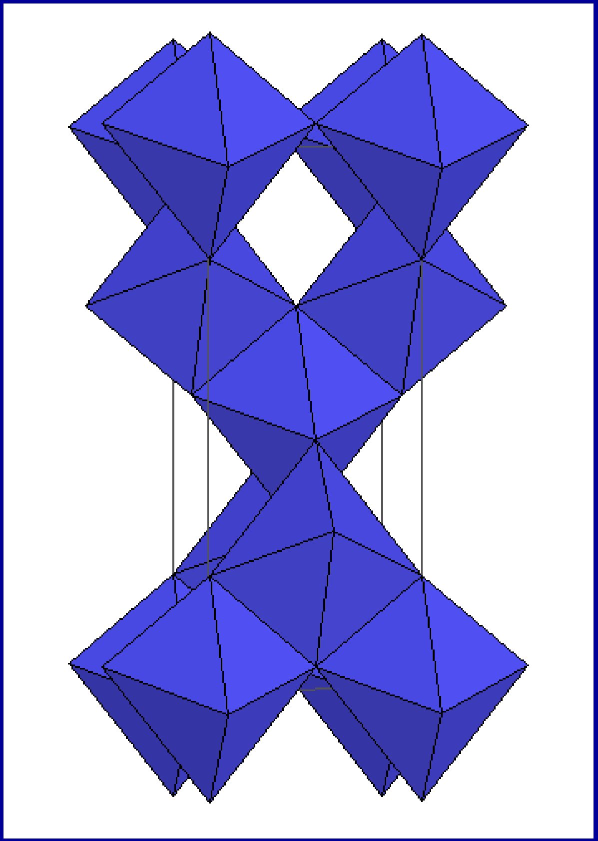
TiO_2: Rutile, Anatase, brookite

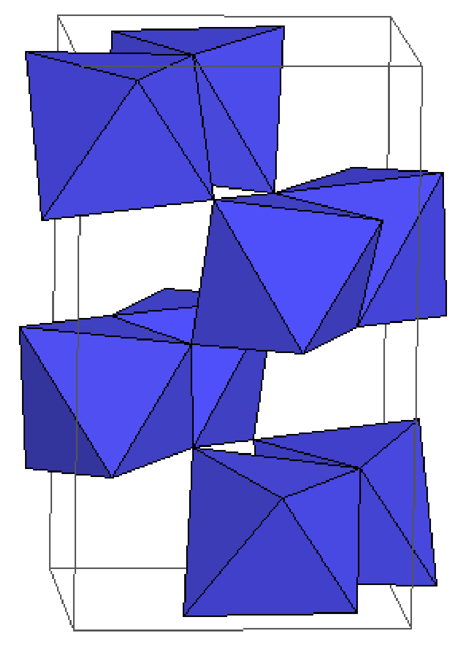


- Tetragonal I (Body-centred tetragonal), $I4_1/amd$
  $a = 3.7845$ Å, $c = 9.5143$ Å; $Z = 4$. (where is the 4_1 screw axis?)
- Less hard and dense than rutile TiO_2.
- Photoactive with well-known application as component of dye-sensitized solar cell (Grätzel cell).

M. Grätzel, *Nature* 1991, **353**, 737.







	Rutile	Anatase	Brookite
Z	2	4	8
Bravias	Tet. P	Tet I	Orth. P
SpaceGroup	$P4_2/mnm$	$I4_1/amd$	Pbca
Vol. (Å^3)	62.07	136.25	257.38

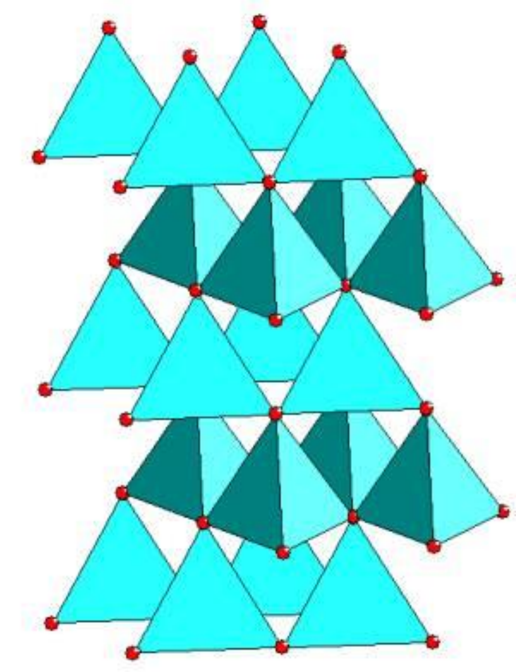
Example 3

Crystal structures of ZnO and SnO_2

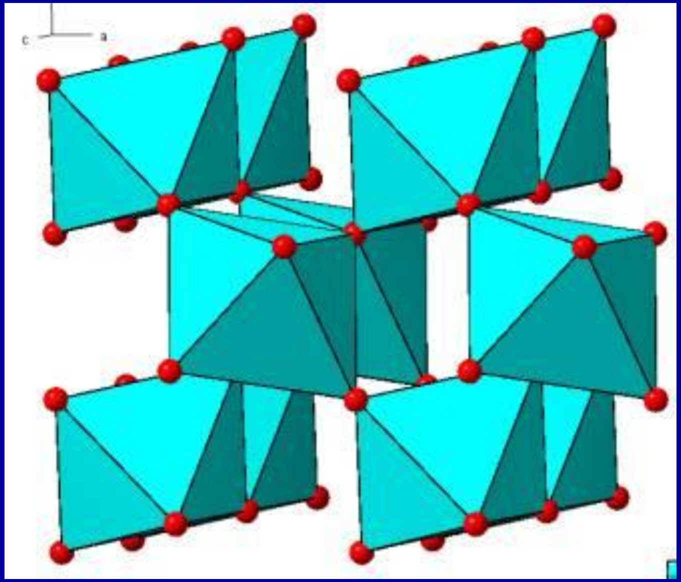
Wurtzite ZnO

Rutile SnO_2

ZnO



Hexagonal , Zn^{2+} :
tetrahedral
coordination



SnO_2

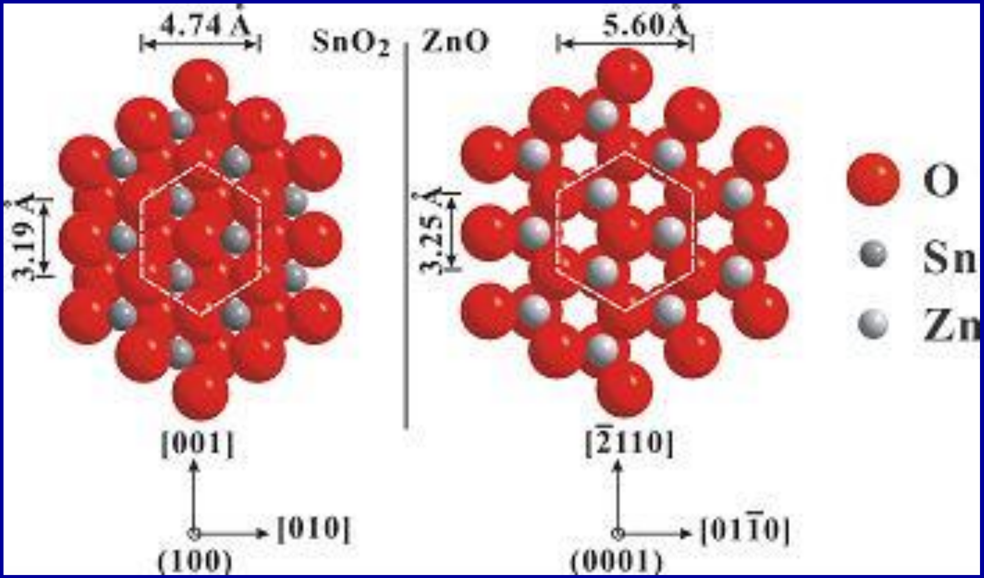
Tetragonal, Sn^{4+} :
octahedral
coordination

Coordination-polyhedra representation of ionic compounds

四方SnO_2

O^{2-}: hexagonal packing

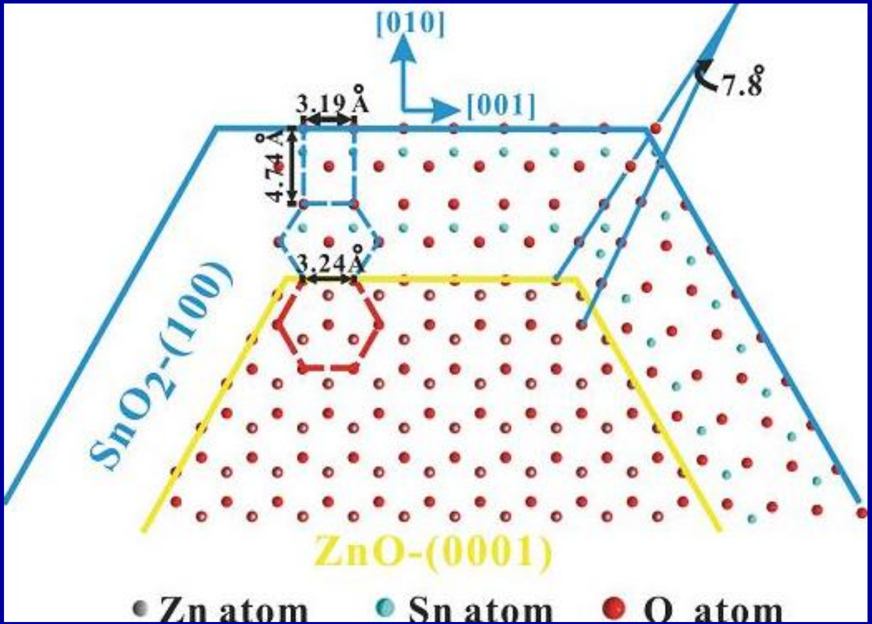
Sn^{4+}:Octahedral interstices



六方ZnO

O^{2-}: hexagonal packing

Zn^{2+}: tetrahedral interstices

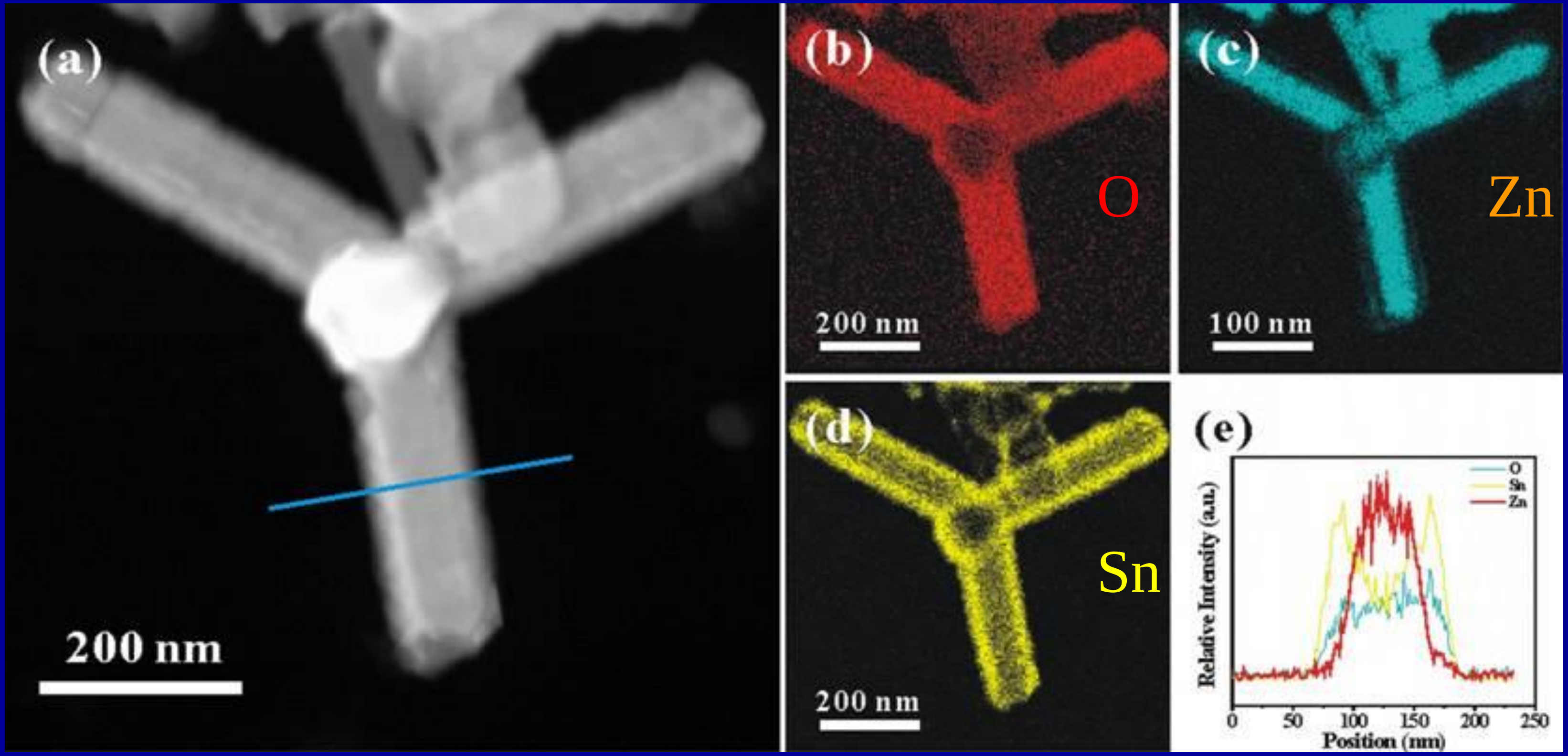


Lattice mismatching is only 1.8% ！

Epitaxial: $(010)_{SnO2} \parallel (0110)_{ZnO}$ and $[100]_{SnO2} \parallel [0001]_{ZnO}$

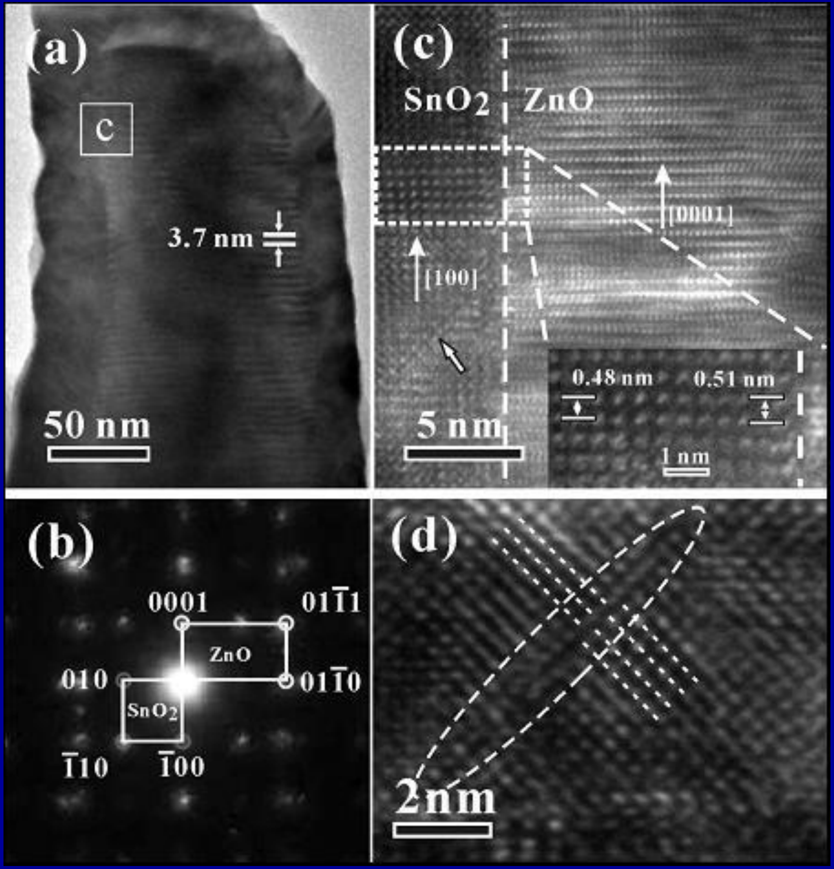
ZnO/SnO_2 heterostructure

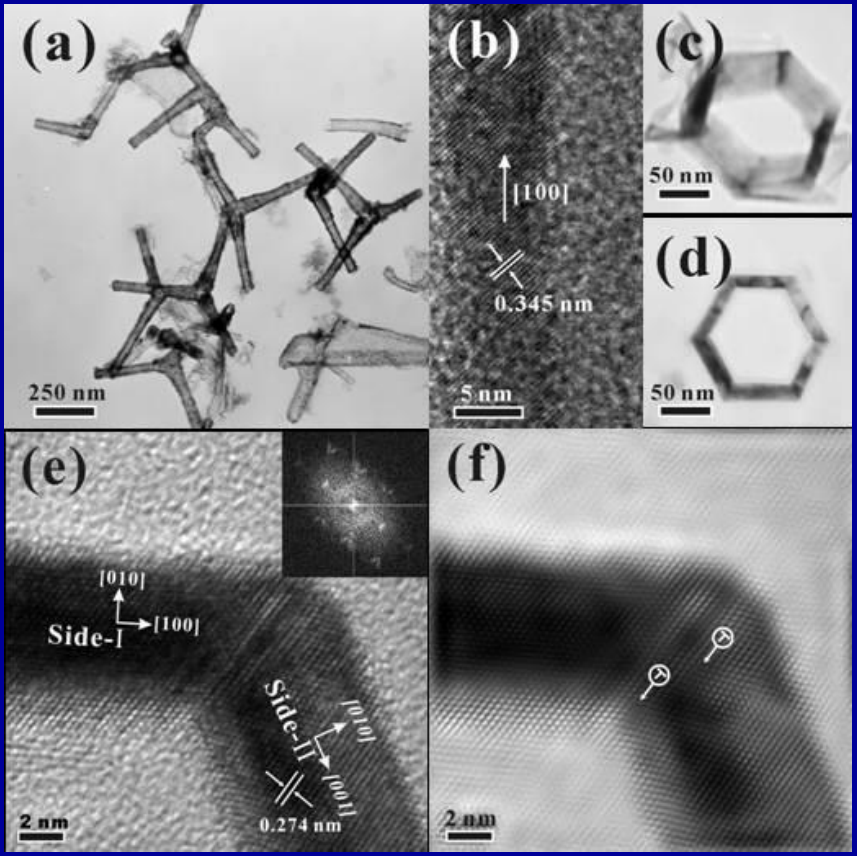
Core-shell structure of tetrapod-like ZnO/SnO$_2$ heterostructure



(SnH$_4$ flow rate = 10 sccm, deposition time = 5 min)

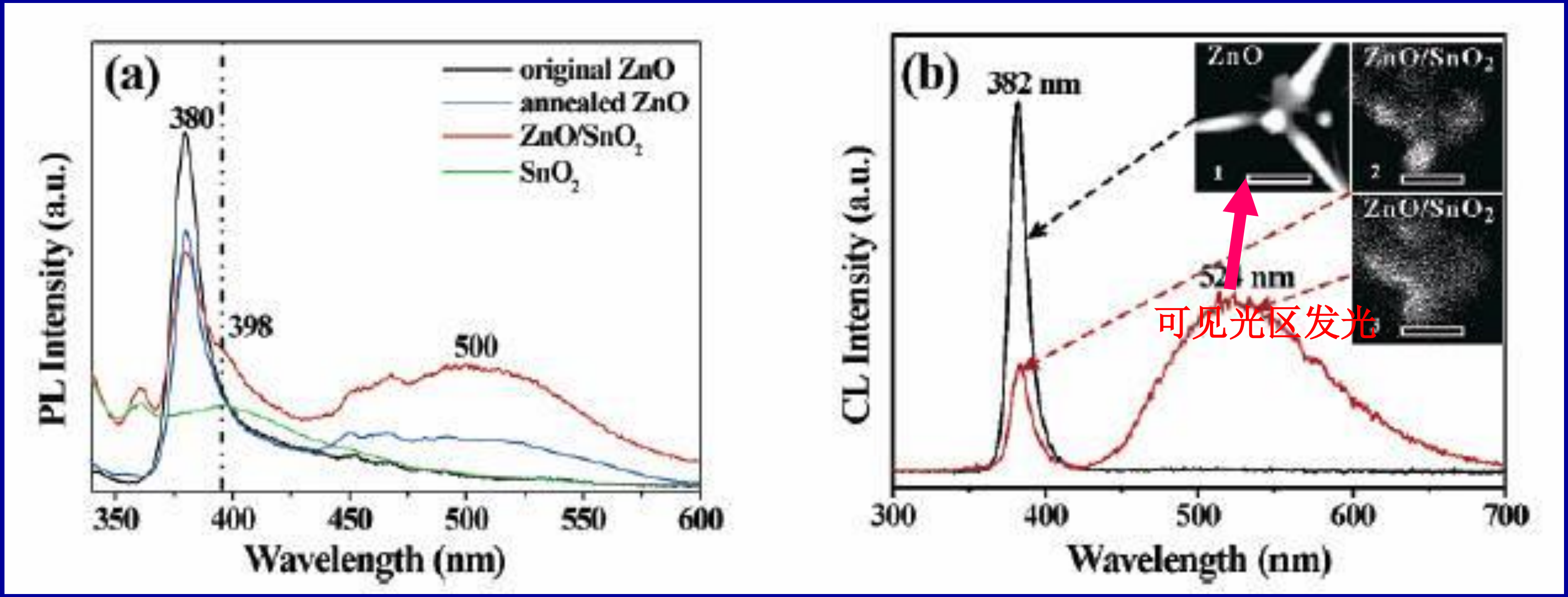
Microstructure of the interface of ZnO/SnO_2 heterostructure





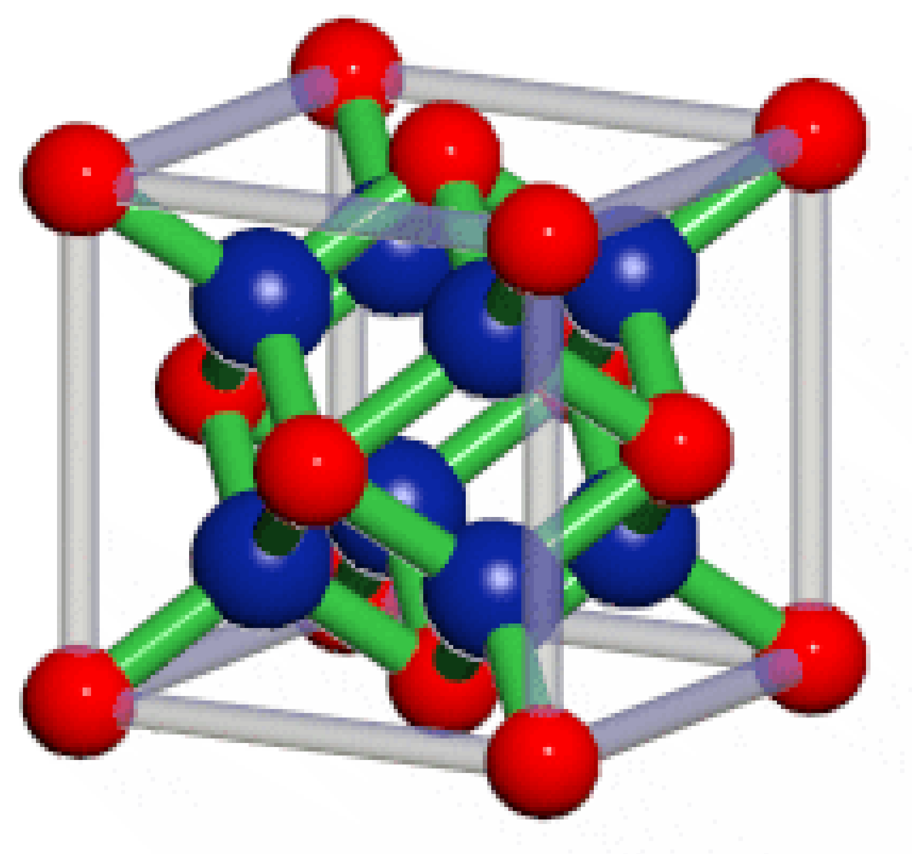
Epitaxial relationship : $(010)_{SnO_2} \parallel (0110)_{ZnO}$ and $[100]_{SnO_2} \parallel [0001]_{ZnO}$

Optical properties of ZnO/SnO_2 heterostructure



- Most of the ionic compound can be described as that cations occupied in the interstices of the close-packing of anions with certain type, and therefore, it is reasonable to design the complicated epitaxial interfaces from the viewpoint of the packing type of anions of ionic crystals.

CaF$_2$ (Fluorite) AB$_2$ type C.N.$^+$:C.N.$^-$ =8:4



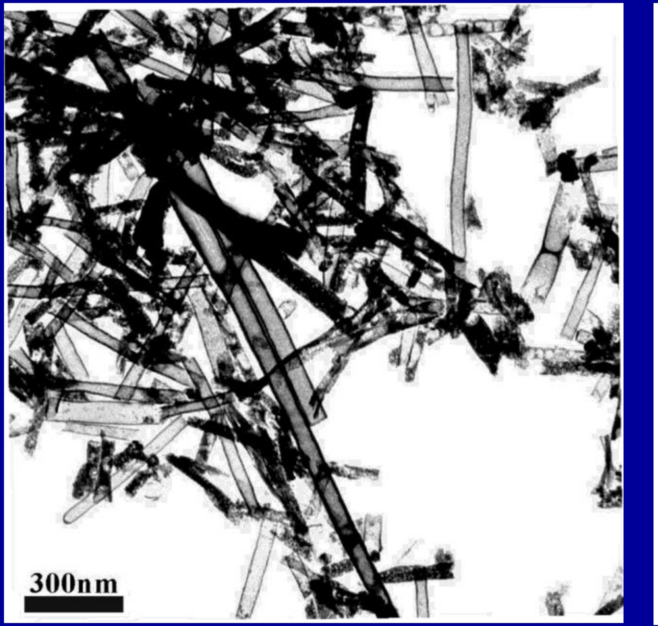
• The packing of anions:	Cubic
•Bravais Lattice :	Cubic F
•The position of cations:	1/2 Cubic holes
The C.N. of cation and anion:	8:4
• Atom number in one unit cell:	Ca:F = 4:8

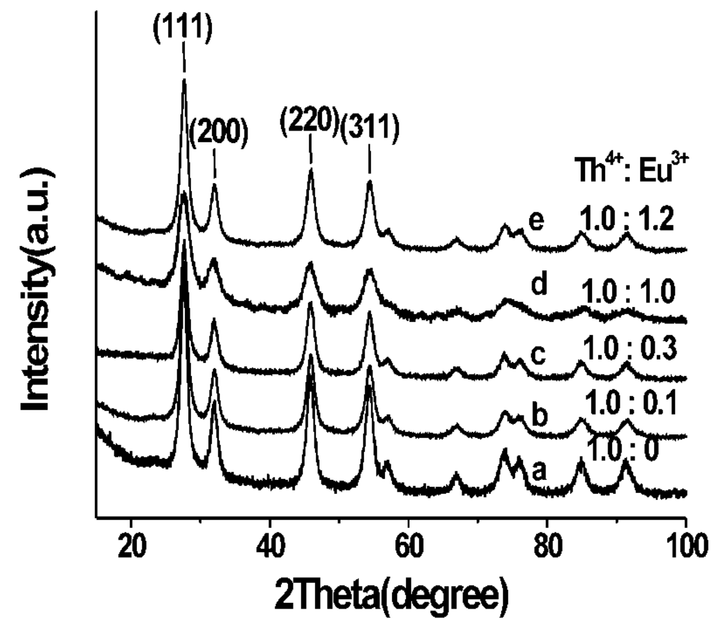
A: 0,0,0; 1/2,1/2,0; 1/2,0,1/2; 0,1/2,1/2 （Ca – red)
B: 3/4,1/4,1/4; 1/4,3/4,1/4; 1/4,1/4,3/4; 3/4,3/4,3/4
3/4,3/4,1/4; 3/4,1/4,1/4; 1/4,3/4,3/4; 3/4,1/4,3/4 (F-deep blue)

($R_+/R_- > 0.732$) BaF$_2$, PbF$_2$, SrF$_2$, HgF$_2$, ThO$_2$, CaF$_2$, UO$_2$, CeO$_2$, PrO$_2$, CdF$_2$; (0.67) ZrF$_2$, HfF$_2$

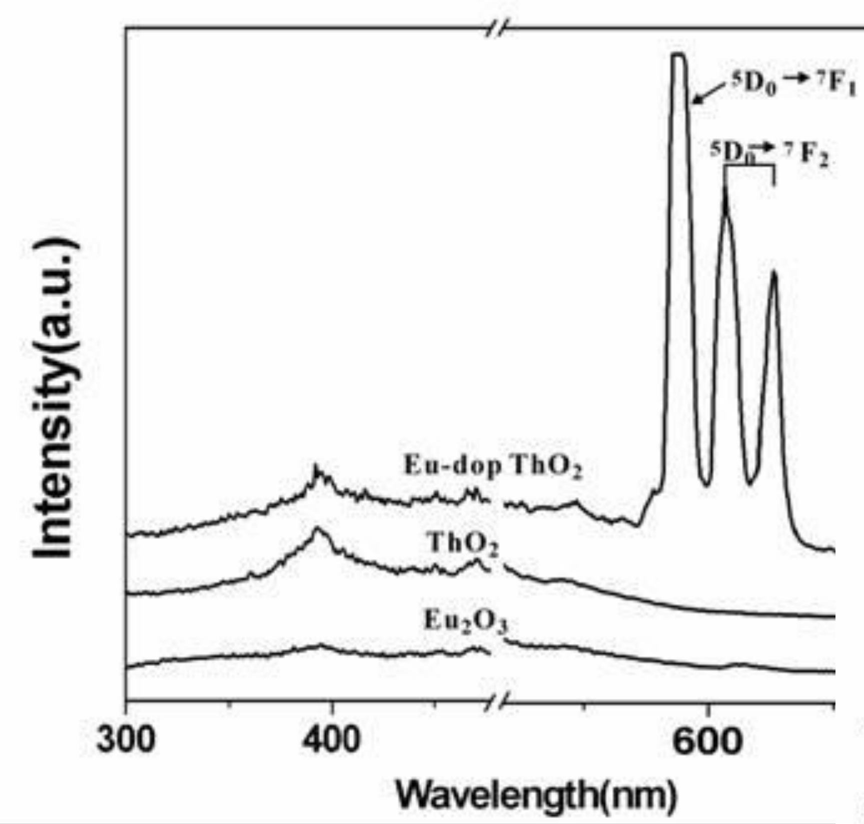
Example 4

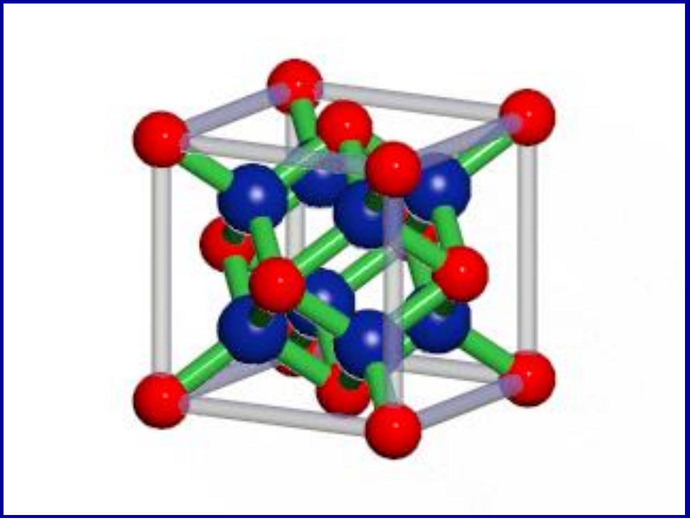
Eu—doped ThO_2

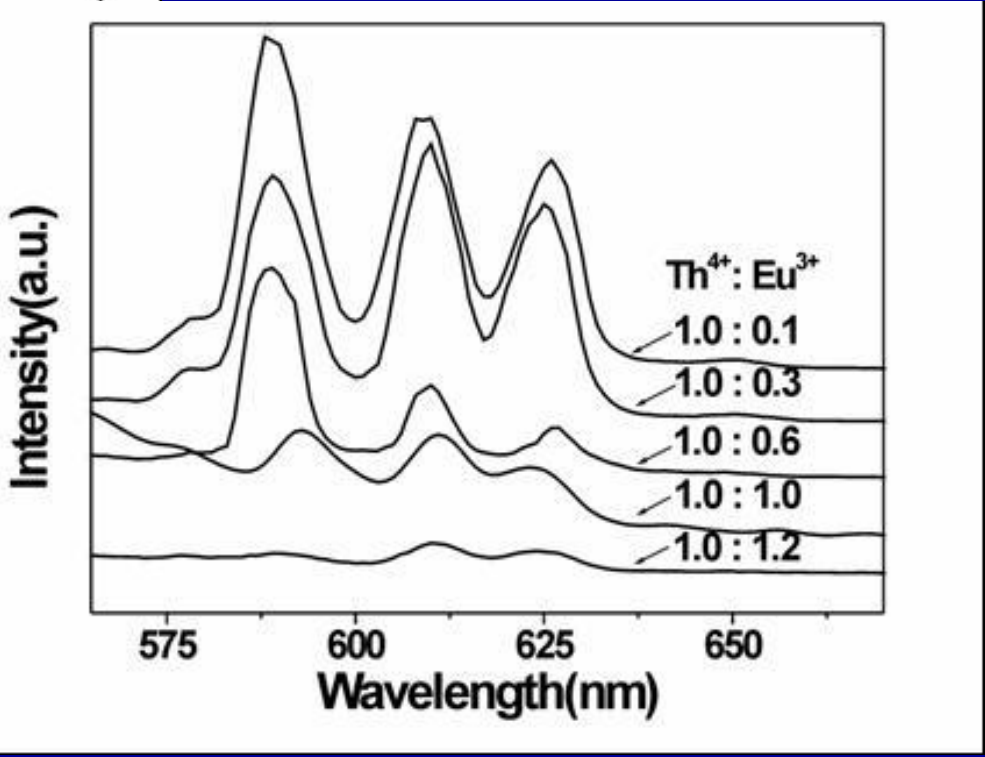




Th^{4+} : Eu^{3+}	1.0 : 0	1.0 : 0.1	1.0 : 0.3	1.0 : 1.0	1.0 : 1.2
a value (nm)	0.5596 ±0.0001	0.5595 ±0.0002	0.5591 ±0.0002	0.5586 ±0.0003	0.5574 ±0.0002





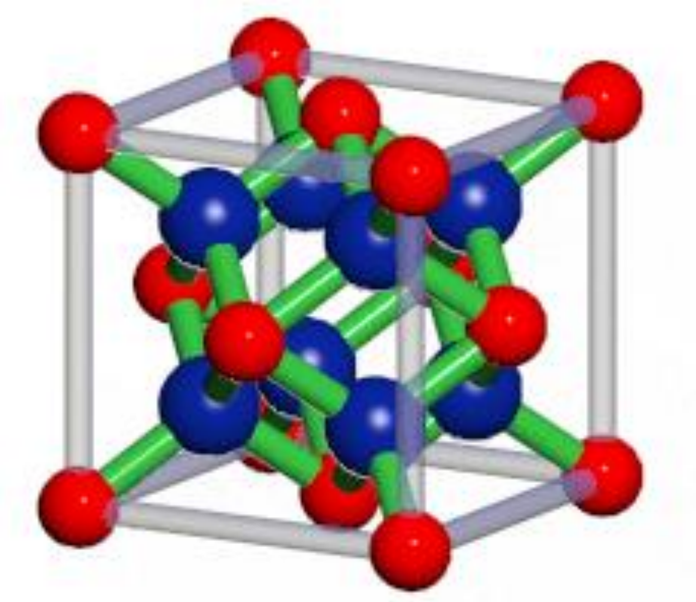


Photoluminescence

Please think about the coordination-polyhedra representation of Fluorite crystal!

- Cubes? Cofacial or co-edge stack?

Rb_2O, Li_2O --- anti-Fluorite structure type



Anions: red

Cations: deep blue

- **The packing of anions: fcc**
- **The position of cations: tetrahedral holes**
- **Bravais Lattice: Cubic F.**
- **The C.N. of anion and cation: 8: 4**
- **Atom number in one unit cell? 4(M_2O)**

Typical Crystal Structures of Binary Component

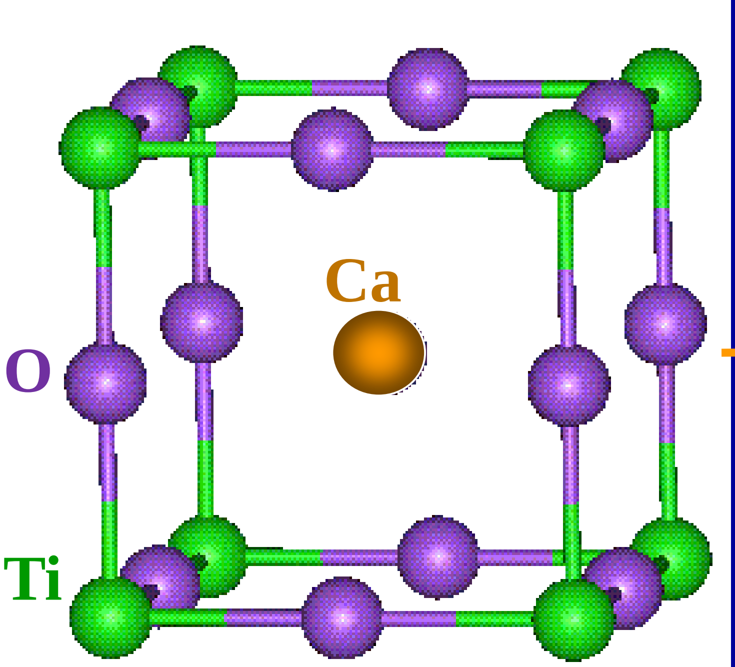
Structure Name	Type	Anion Packing	Lattice Type	Cation position	Coordination Numbers		Examples
					Cations	Anions	
Soldium Chloride	AB	FCC	C-F	All octahedral holes	6	6	NaCl, MgO, FeO,LiF, CaO, NiO
Cesium chloride	AB	Simple cubic	C-P	All cubic holes	8	8	CsCl
Zinc blende (sphalerite)	AB	FCC	C-F	1/2 tetrahedral holes	4	4	ZnS, SiC
Wurzite	AB	HCP	H-P	1/2 tetrahedral holes	4	4	ZnS
Fluorite	AB_2	Simple cubic	C-F	1/2 cubic holes	8	4	CaF_2,ZrO_2
Anti-Fluorite	A_2B	FCC	FCC	All tetrahedral holes	4	8	Li_2O
Rutile	AB_2	HCP	T-P	1/2 octahedral holes	6	3	TiO_2, MnO_2, SnO_2

9.2.2 Ternary and more complicated ionic compounds

a) $CaTiO_3$ -- perovskite -- ABX_3

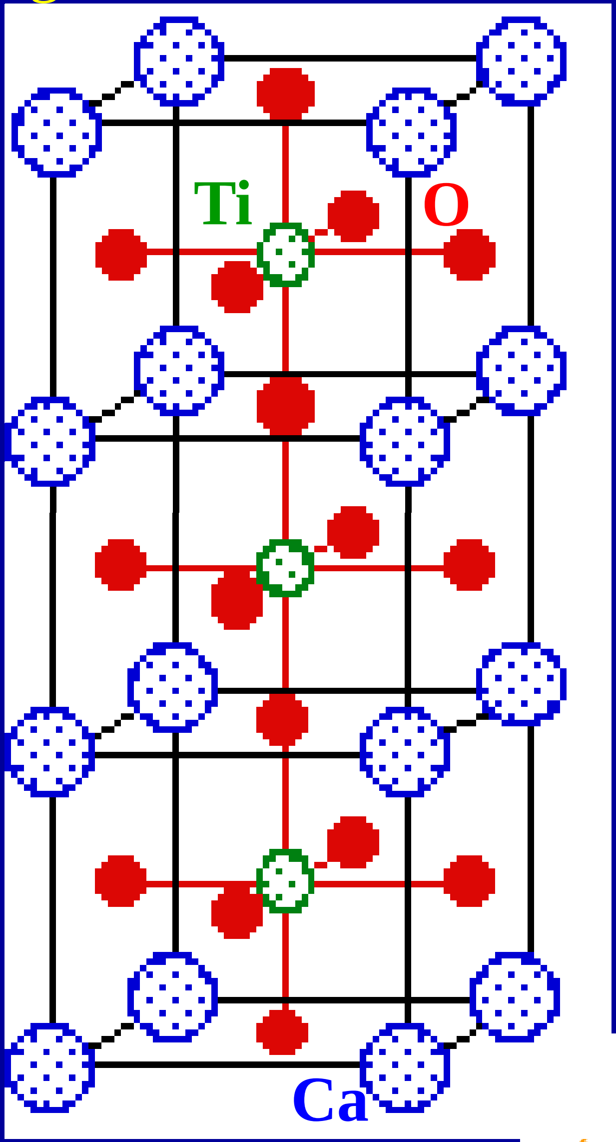
Ideally ***cubic***, but actually tetragonal or orthorhombic!

Cubic-P



1. Shift of origin to Ca.

2. Stacking of 3 cubic units

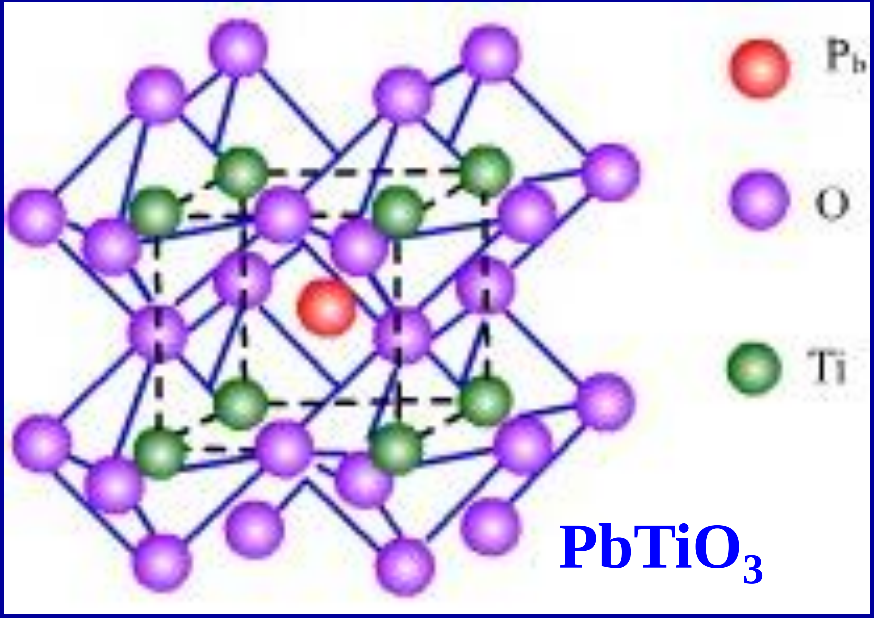


O (X): “ccp/fcc” (4) – (1) = (3)

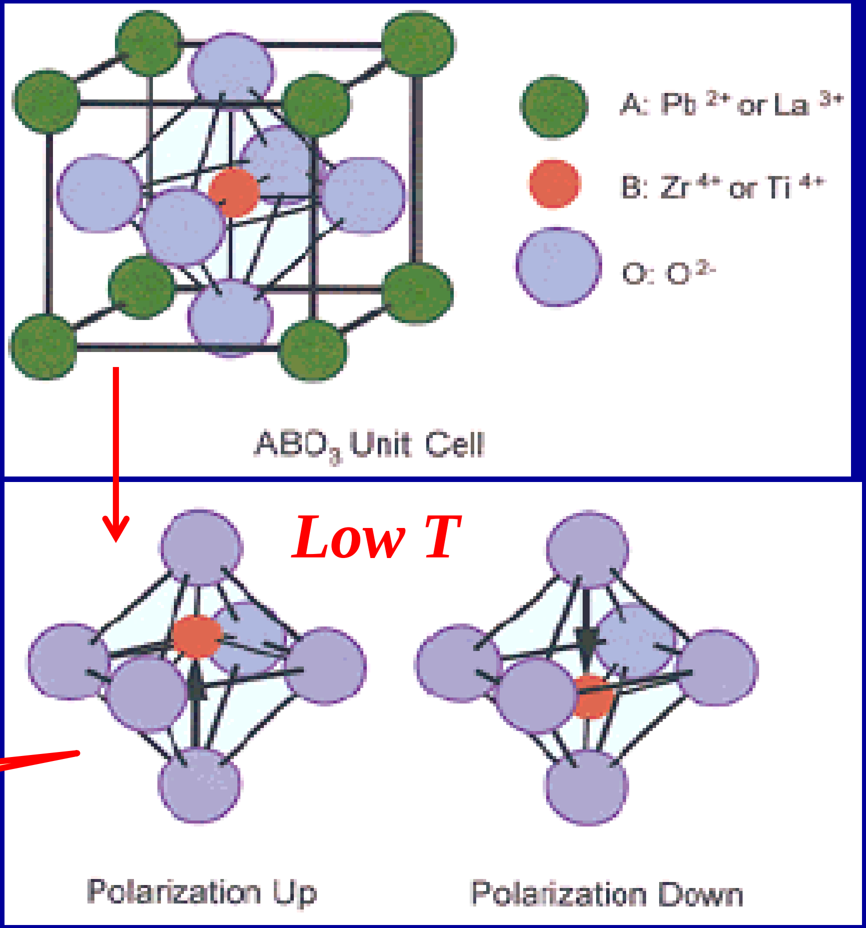
Ti (B): 1/4 octahedral holes (1)

Ca(A): cuboctahedral hole (1)

Perovskite structure and Ferroelectric effect



- **High T, cubic P, non-polar phase (paraelectric!) μ*(total) =0***



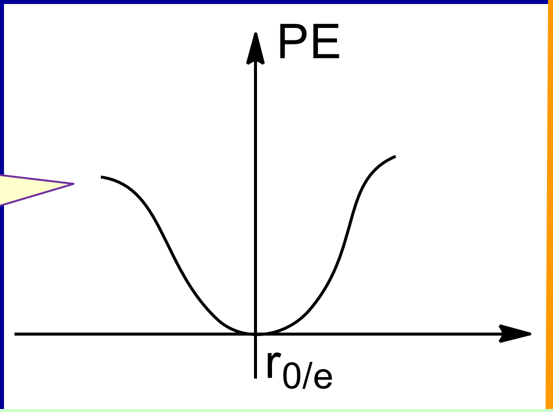
- **Low T, tetragonal, spontaneous polarization, overall polarity, μ*(total) $\neq$ 0!***

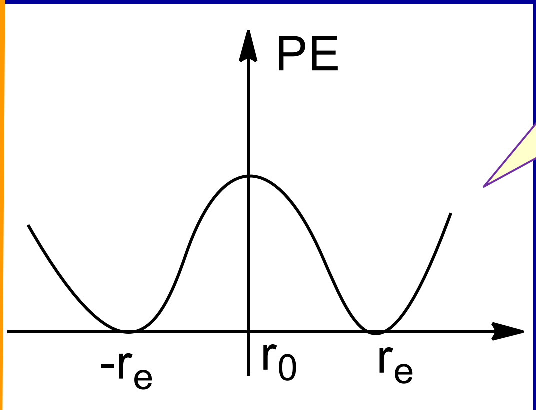
Two polar phases with distorted octahedra around the B cations!

Potential energy surfaces of two phases of Ferroelectric solid

- No spontaneous polarization
- Spontaneous polarization

Non-polar phase



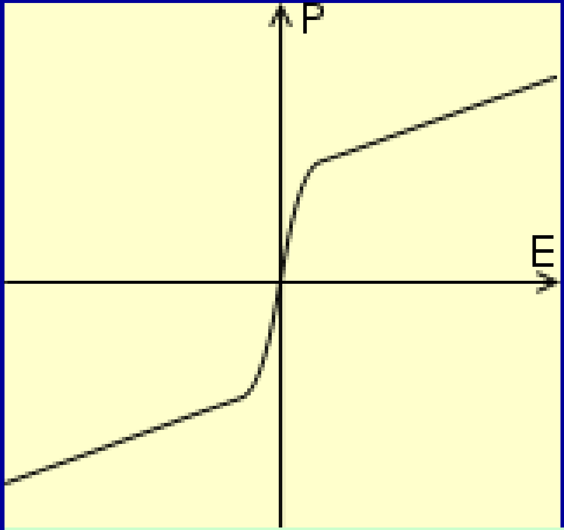


Polar phase

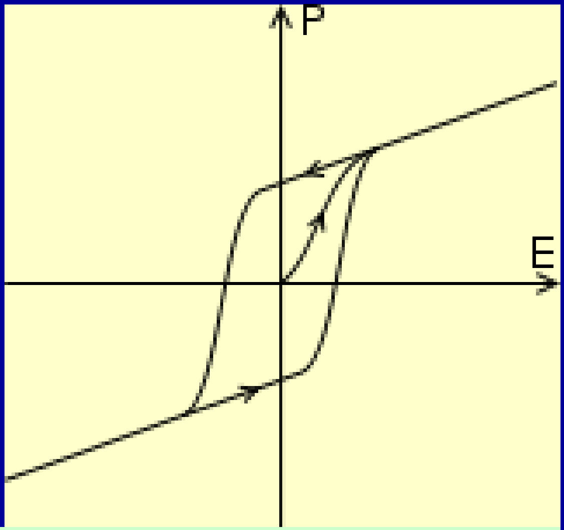
r_0: the center of octahedron

Potential energy surface (no external field)

- Paraelectric polarization

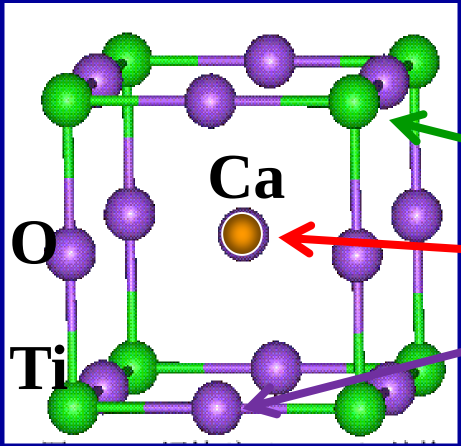


- Ferroelectric polarization



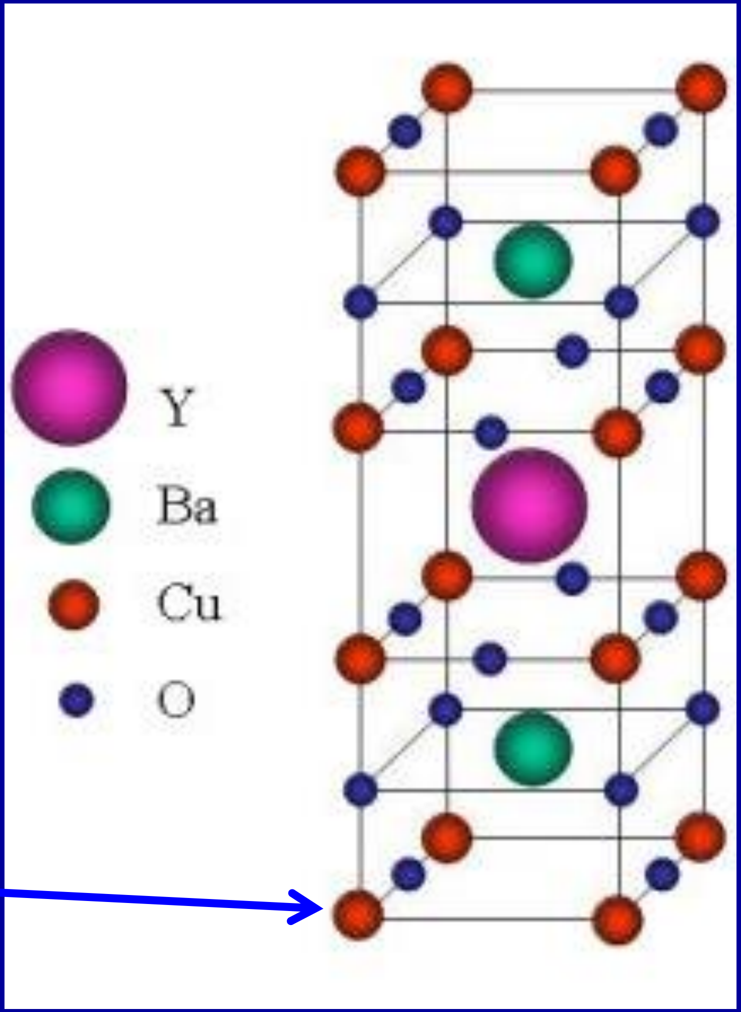
External field induced polarization!

Perovskite structure and H-T superconductor



- Substitution of Cu^{n+}
- Doping of Y^{3+} & Ba^{2+}
- Partial loss of O^{2-}

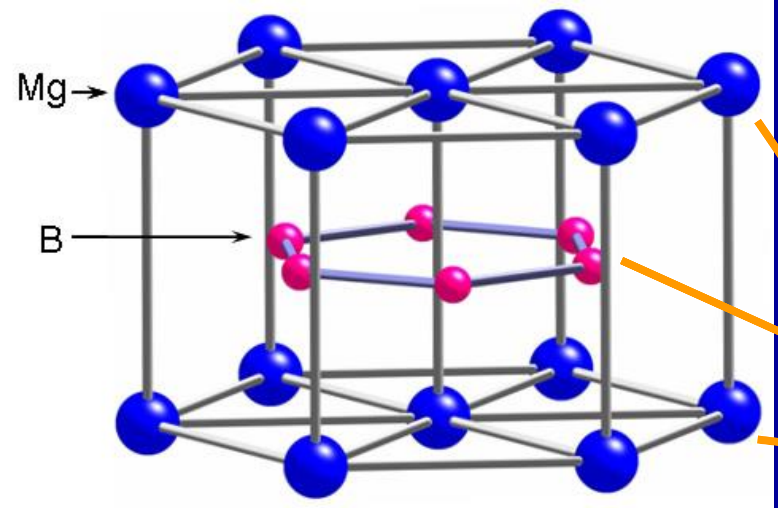
- 1986, Bednorz and Müller at IBM Zurich discovered the Y-Ba-Cu-O solid exhibits superconductivity up to 93 K.
- ***x=0***: Mixture of Cu^{2+} and Cu^{3+}.
- Up to now, related oxides exhibits superconductivity up to 125 K.

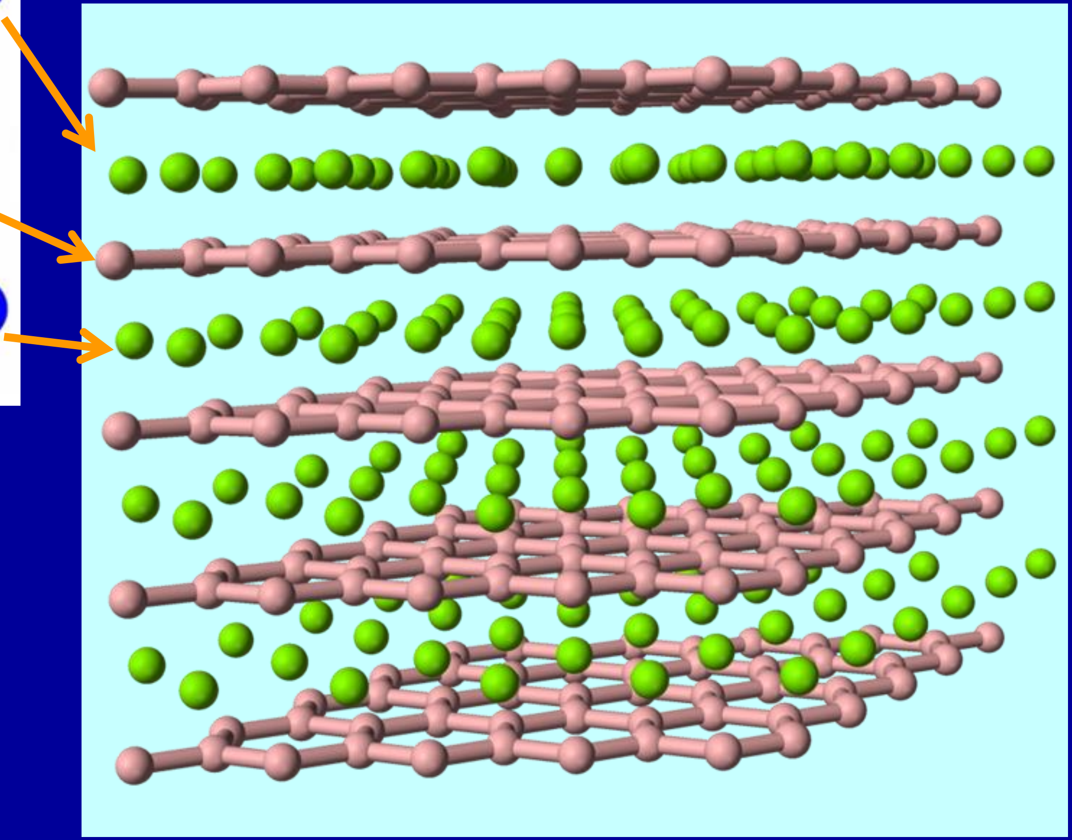


$YBa_2Cu_3O_{7-x}$

- Tetragonal or orthorhombic

Another type of HT superconductive solid – MgB_2





- First synthesized in 1953.
- HTS (Tc ~39K) discovered in 2001.
- Lattice: Hexagonal hP3
- Space Group: P6/mmm

Conventional superconductivity at 203 kelvin at high pressures in the sulfur hydride system

P > ~150Gpa, **H_2S (s) → ? ! H_3S (s)**

Drozdov et al., Nature, 2015, 525, 73.

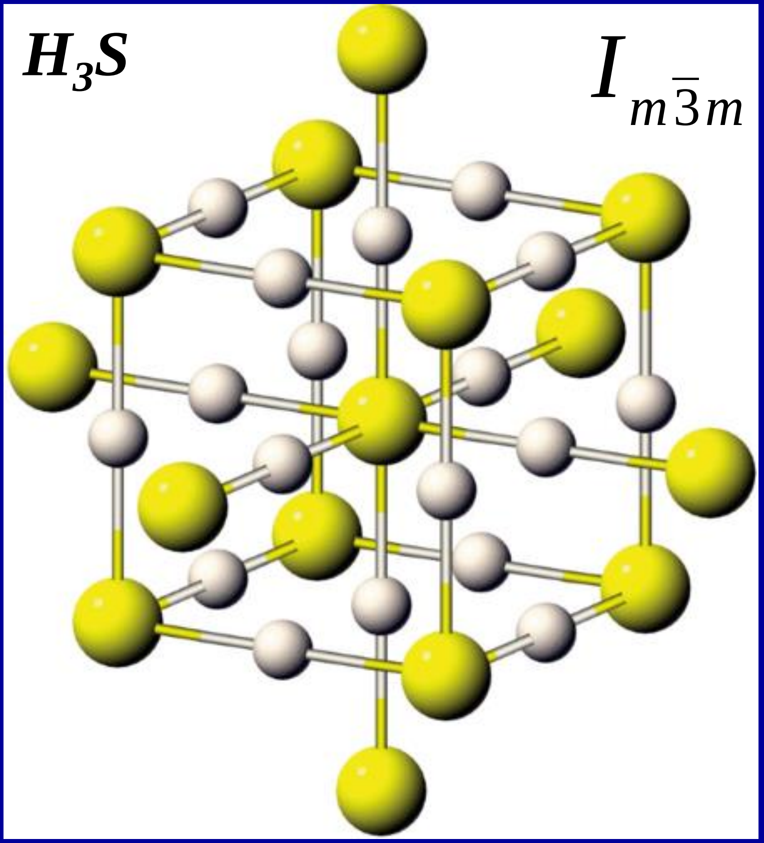
2015 Nature's 10

Theoretical predictions:

P > 180Gpa,

$(H_2S)H_2$ (s) → H_3S (s)

$T_c > \sim 200K$



Strobel T A et al, Phys Rev Lett, 2011, 114, 157004;

Cui T et al, Sci. Rep. 2014, 4, 6968; Phys. Rev. B 2015, 91, 180502(R)

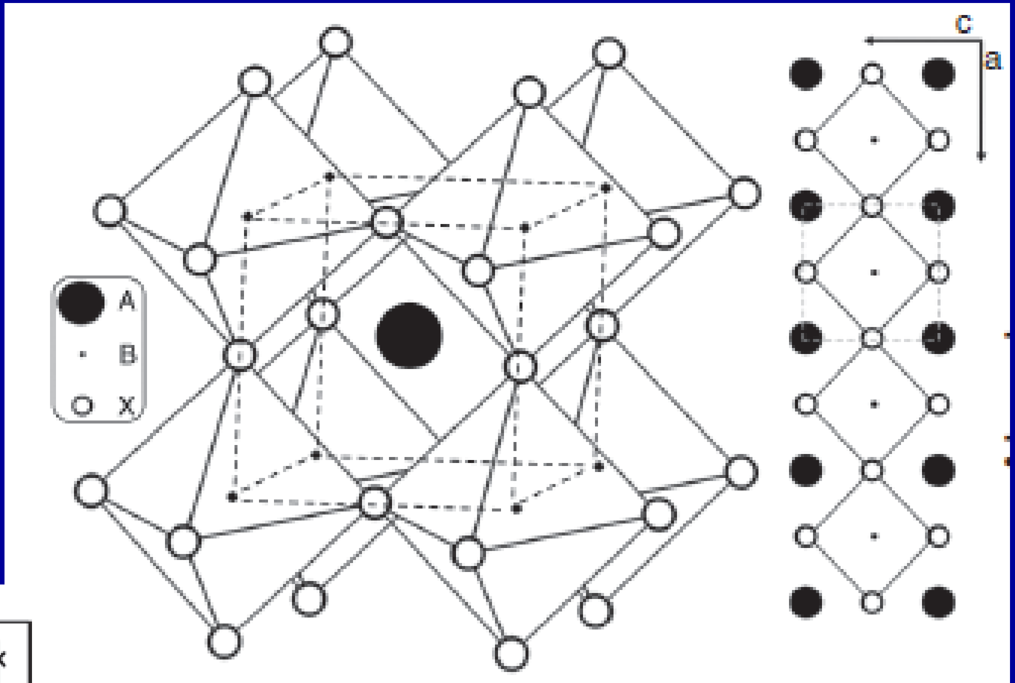
Photoactive Organometal Halide Perovskite ABX_3 in Meso-superstructured Solar Cell (MSSC).

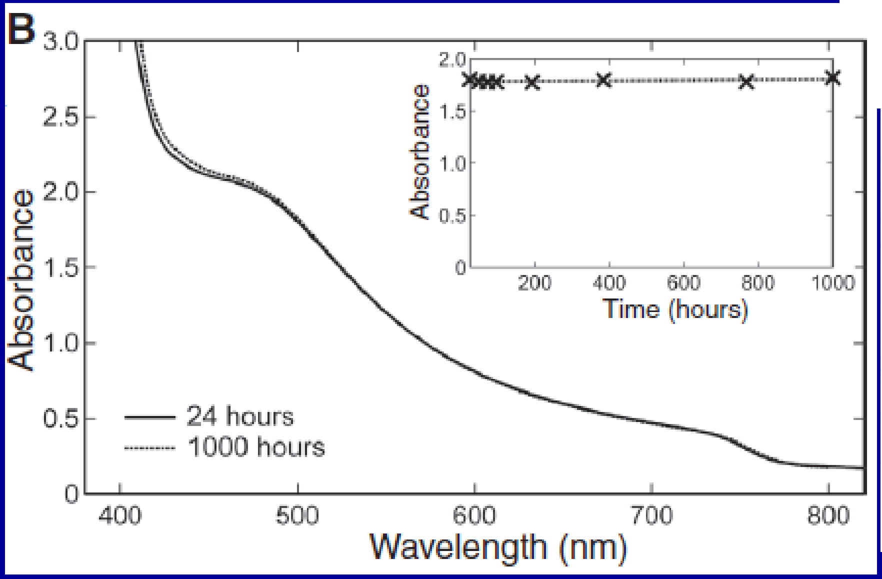
Snaith et al., Science, 2012, 338, 643.

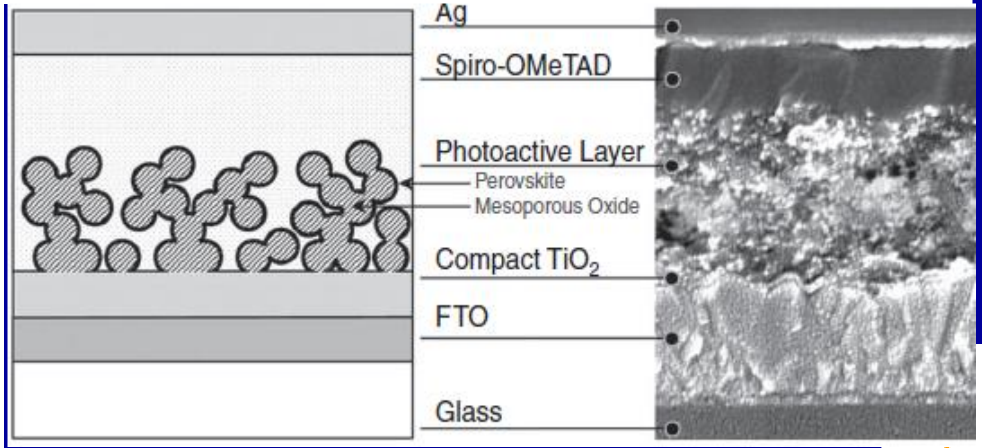
Photoactive $CH_3NH_3PbI_3$

$A = [CH_3NH_3]^+$
$B = Pb^{2+}$,
$X = I$

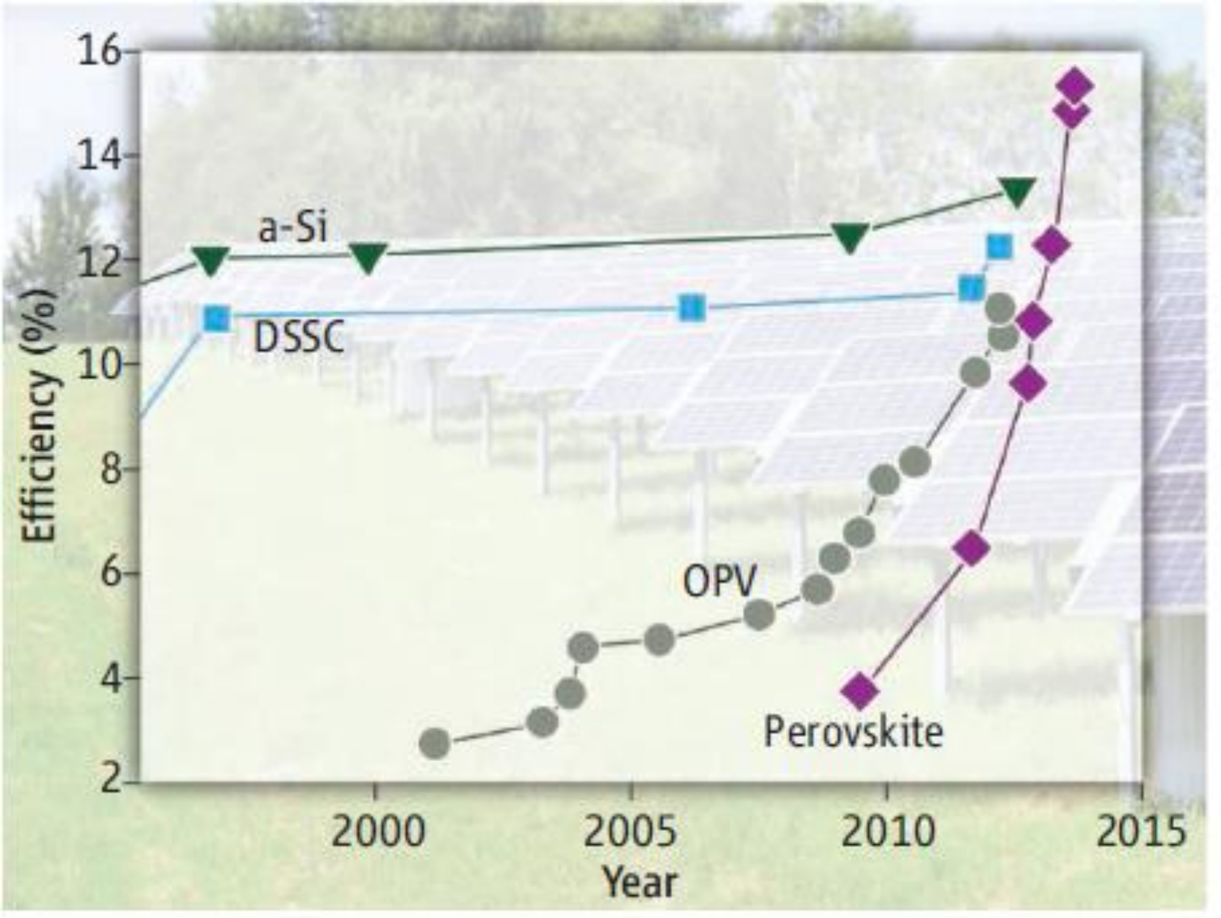
- Broad band of absorption.
- Optimal power conversion efficiency ~ 10.9%.







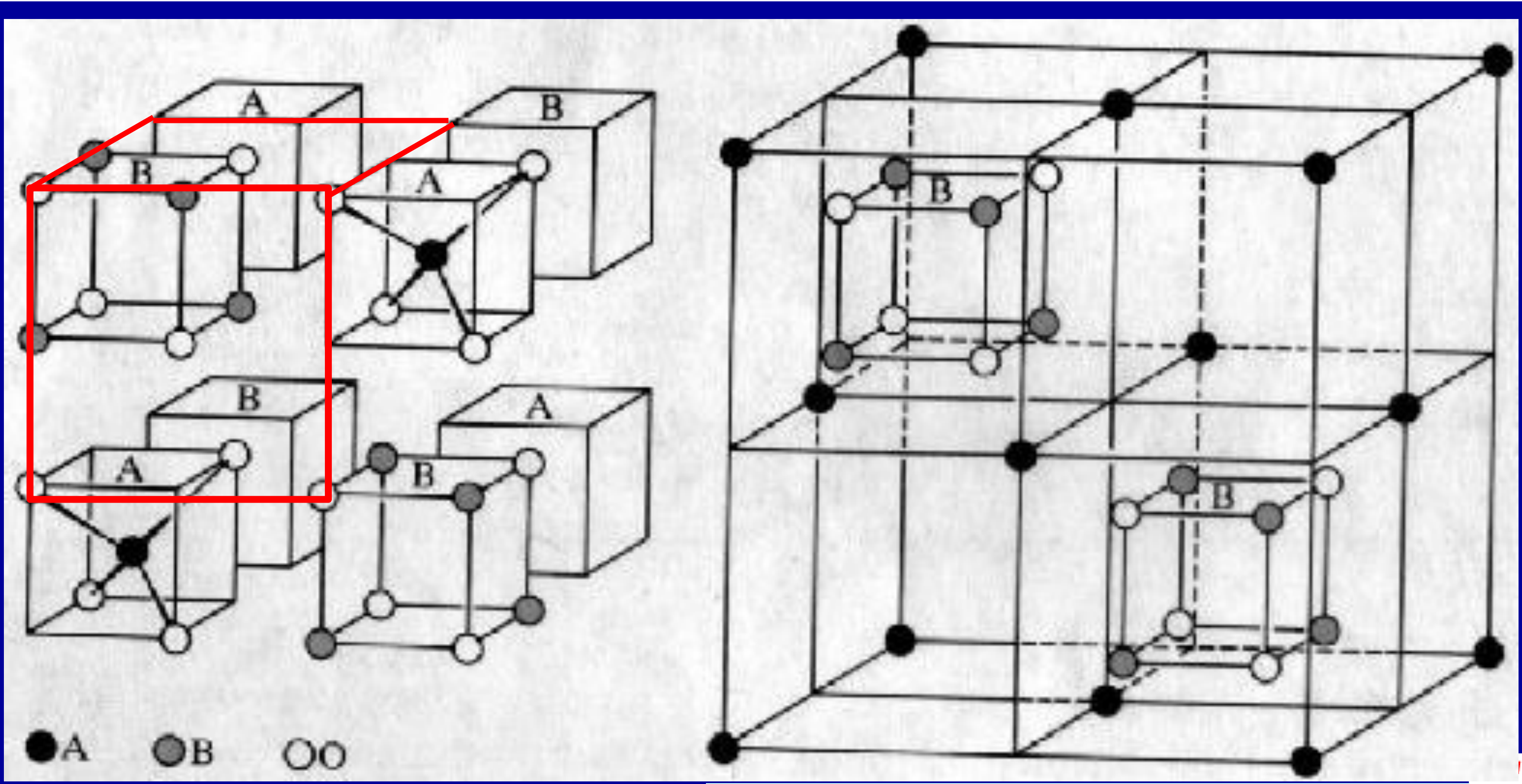
Perovskite-based Solar Cell.



- Up to now, the Perovsite-based Solar Cell can reach an optimal efficiency **~ 20%**, higher than that of commercial a-Si solar cell.
- Its drawback: not water-resistant at all!

$MgAl_2O_4$ (spinel) AB_2X_4 Lattice type: Cubic-P

- O anions form fcc lattice (2x2x2 of O-fcc cells, O: 8x4=32)
- Mg^{2+}cations (A) in 1/8 tetrahedral holes (8x8/8); Al^{3+} cations (B) in half of octahedral holes (8x4/2) → **A:B:O = 8:16:32**



Unit cell: too large

eg. $FeAl_2O_4$, $ZnAl_2O_4$, $MgAl_2O_4$

http://www.chemtube3d.com/solidstate/_spinel(final).htm

Spinel crystals

anti-spinel $B[AB]O_4$ --- the Magnetic property

magnetite (Fe_3O_4) = spinel ($Fe^{3+}(Fe^{3+},Fe^{2+})O_4$ = $B(AB)O_4$

O anions form fcc lattice

Fe^{3+} (B) cations in 1/8 tetrahedral holes,

(Fe^{2+}, Fe^{3+}) (AB) cations in half of octahedral holes

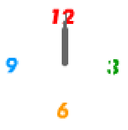
Spinel $[A]_t[BB]_oO_4$

Anti-spinel $[B]_t[AB]_oO_4$

eg. $FeFe_2O_4$, $FeMgFeO_4$

Summary of Some Common Crystal Structures

Structure Name	Structure Type	Anion Packing	Cation position	Coordination Numbers		Examples
				Cations	Anions	
Rock Salt	AB	FCC	All octahedral holes	6	6	NaCl, MgO, FeO,LiF, CaO, NiO
Cesium chloride	AB	Simple cubic	All cubic holes	8	8	CsCl
Zinc blende (sphalerite)	AB	FCC	1/2 tetrahedral holes	4	4	ZnS, SiC
Wurtize	AB	HCP	1/2 tetrahedral holes	4	4	ZnS
Fluorite	AB2	Simple cubic	1/2 cubic holes	8	4	CaF_2,ZrO_2
Rutile	AB2	HCP	1/2 tetrahedral holes	6	3	TiO_2, MnO_2, SnO_2
Perovskite	ABX_3	FCC(A and X)	All octahedral holes for B	12(A) 6(B)	6	$BaTiO_3$, $SrTiO_3$
Spinel	AB_2X_4	FCC	1/8 octahedral holes for A 1/2 tetrahedral holes	4(A) 6(B)	4	$MgAl_2O_4$ $FeAl_2O_4$



9.3 Lattice energy

The calculation and determination of lattice energy

$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) + U$(Lattice Energy)

Overall electrostatic interaction energy exerted on a cation

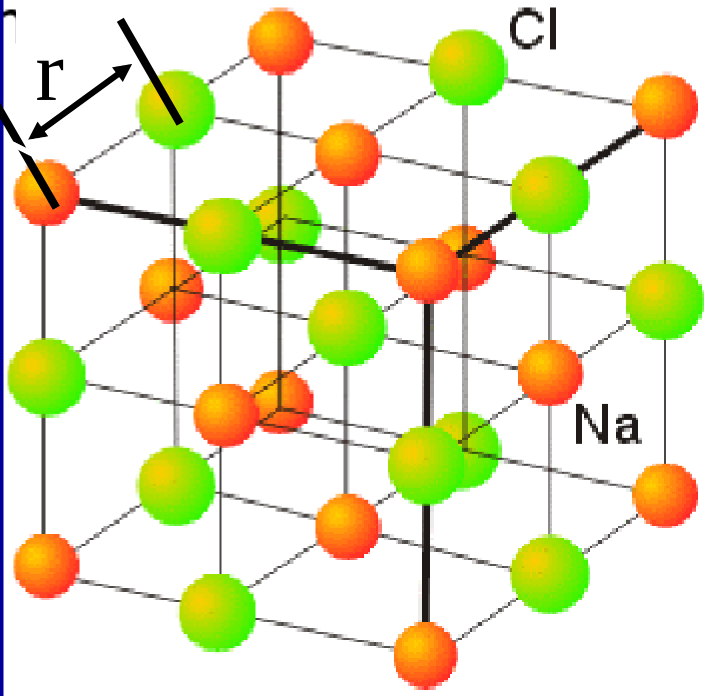
$$\varepsilon(Na^+) = \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}[6+\frac{12}{\sqrt{2}}\frac{Z_+}{Z_-}+\frac{8}{\sqrt{3}}+\frac{6}{\sqrt{4}}\frac{Z_+}{Z_-}+\ldots]$$

$$= \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}[6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\ldots]$$

$$= \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}A, \quad A = [6-\frac{12}{\sqrt{2}}+\frac{8}{\sqrt{3}}-\frac{6}{\sqrt{4}}+\ldots]$$

Structure-dependent

$A \approx 1.7476$, Madelung constant of NaCl-type



$$EP(Na^+) = \frac{Z_-e}{4\pi\varepsilon_0 r}A$$

Point-charge model!

Madelung potential on a cation!

$$\varepsilon(Na^+) = \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}A$$

$A \approx 1.7476$, Madelung constant

Similarly,

$$\varepsilon(Cl^-) = \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}A$$

Total ion-ion attraction energy:

$$E_c = \frac{N_A}{2}[\varepsilon(Na^+) + \varepsilon(Cl^-)]$$

$$= \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}AN_A$$

Ion-ion pauli repulsion:

$$\varepsilon_R = Br^{-m} \Rightarrow E_R = N_A Br^{-m}$$

Lattice energy

$$U = Ec + E_R = \frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r}AN_A + N_A Br^{-m}$$

（**B** is unknown yet!)

$$\left(\frac{\partial U}{\partial r}\right)_{r=re} = -\frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r_e^2}AN_A - \frac{mN_A B}{r_e^{m+1}} = 0$$

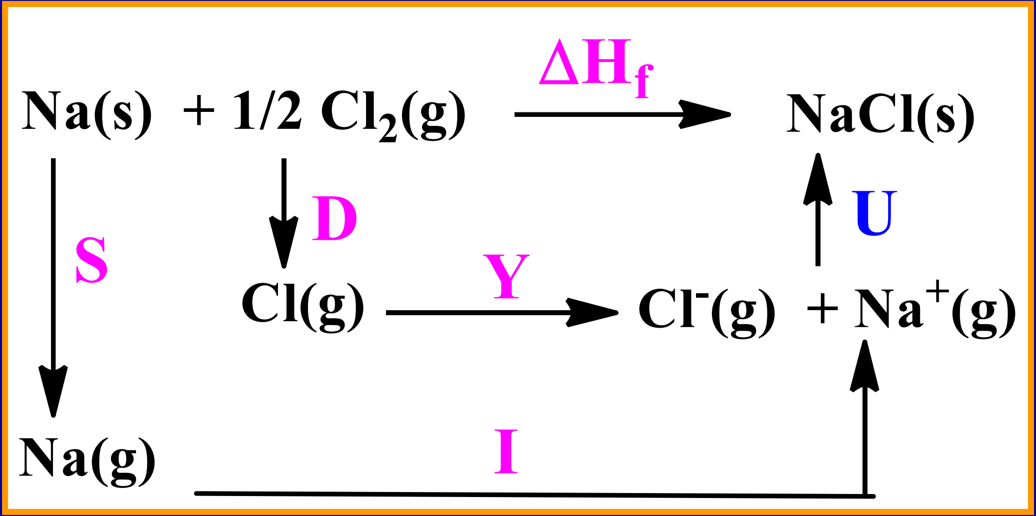
$$\Rightarrow B = -\frac{Z_+Z_-e^2A}{m4\pi\varepsilon_0}r_e^{m-1}$$

$$U = \frac{N_A Z_+Z_-e^2A}{4\pi\varepsilon_0 r_e}\left(1 - \frac{1}{m}\right)$$

NaCl: m = 8, r_e = 2.8197*10^{-10}m

U = -753 kJ/mol

The lattice energy calculated from the Born-Haber cycle (Experimental determination)



$$\begin{tikzcd}
\mathrm{Na(s)} \arrow[dd, "S"] & +\ 1/2\ \mathrm{Cl_2(g)} \arrow[rr, "\Delta H_f"] \arrow[d, "D"] & & \mathrm{NaCl(s)} \\
 & \mathrm{Cl(g)} \arrow[r, "Y"] & \mathrm{Cl^-(g)} & +\ \mathrm{Na^+(g)} \arrow[u, "U"] \\
\mathrm{Na(g)} \arrow[rrru, "I"] & & &
\end{tikzcd}$$

1) $\mathrm{Na(s)} \rightarrow \mathrm{Na(g)}$ $S = +108.4\ \mathrm{kJ.mol^{-1}}$

2) $\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + e$ $I = +495.0\mathrm{kJ.mol^{-1}}$

3) $1/2\mathrm{Cl_2(g)} \rightarrow \mathrm{Cl(g)}$ $D = +119.6\mathrm{kJ.mol^{-1}}$

4) $\mathrm{Cl(g)} + e \rightarrow \mathrm{Cl^-(g)}$ $Y = -348.3\ \mathrm{kJ.mol^{-1}}$

5) $\mathrm{Na(s)} + 1/2\ \mathrm{Cl_2(g)} \rightarrow \mathrm{NaCl}$ $\Delta H_f = -410.9\ \mathrm{kJ.mol^{-1}}$

→ $\Delta H_f = S + I + D + Y + U$ (to be determined!)

→ $U = \Delta H_f - (S + I + D + Y) = -785.6\ \mathrm{kJ.mol^{-1}}$

9.4 Ionic radii

9.4.1 How to determine ionic radii

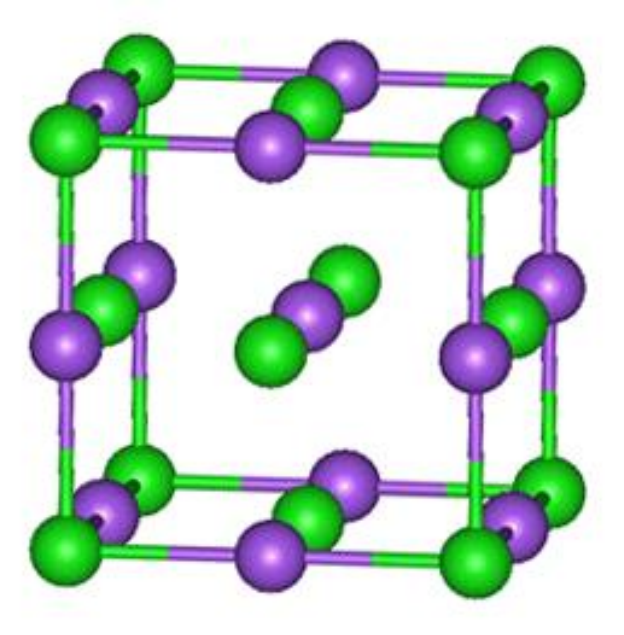
Lande: (1920)

- The cell parameters for MnS and MgS (**a=5.2 Å**) as well as MgSe and MnSe (**a=5.46 Å**, NaCl-type) are nearly identical.
- Lande suggested that the anions in the structure were contacted with one another. Then

$$4r_{anion} = \sqrt{2}a \Rightarrow r_{anion} = \sqrt{2}a/4$$

$$r_{S^{2-}} = 2.60/\sqrt{2} = 1.84\dot{A}$$

$$r_{Se^{2-}} = 2.73/\sqrt{2} = 1.93\dot{A}$$



Pauling (1927):

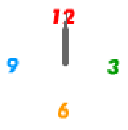
- Pauling deduced many ionic radii from the internuclear separations of five different crystal (NaF, KCl, RbBr, CsI and Li_2O) using a semi-empirical method.
- The size of an atom are determined by the valence sell electron distribution which is inversely proportional to the effective nuclear charge.

$$r = c_n/(Z-\sigma) = c_n/Z^*$$

c_n is a constant dependent on the principal quantum number ***n***.

for NaF: by Slater rule $\sigma = 2x0.85 + 8x0.35 = 4.5$

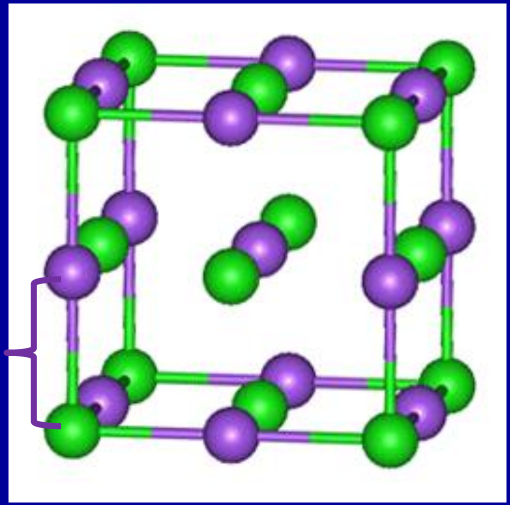
Pauling gave σ a value of 4.52 for Ne type ions;



$$r_{Na^+} = c_n/(11-4.52)$$

$$r_{F^-} = c_n/(9-4.52)$$

$$\because r_{Na^+} + r_{F^-} = a/2$$



***a* =4.62 Å** - the cell parameter of NaCl.

$$\therefore r_{Na^+} = 0.95; \quad r_{F^-} = 1.36; \quad c_n = 6.15$$

From the value of c_n, one can calculate the radii of all univalent Ne-like ions. However, for divalent ions, for example,

$$r_{Mg^{2+}} = 6.15/(12-4.52) = 0.82; \quad r_{O^{2-}} = 1.76$$

leading to unreasonable prediction

$$r_{Mg^{2+}} + \quad r_{O^{2-}} = 2.58 >> 2.10A \quad (\text{exptl. value})$$

Hence, correction based on the charge state is required for those multiply-charged ions.

Let’s consider the expression of lattice energy at equilibrium structure,

$$\left(\frac{\partial U}{\partial r}\right)_{r=re} = -\frac{Z_+Z_-e^2}{4\pi\varepsilon_0 r_e^2}AN_A - \frac{mN_AB}{r_e^{m+1}} = 0$$

$$\Rightarrow -mB = [Z_+Z_-e^2A][r_e^{m-1}]/(4\pi\varepsilon_0)$$

For NaCl-type structures (e.g., NaCl and MgO), mB value remains to be a constant. Thus

$$Z^2 r_z^{m-1} = 1^2 r_1^{m-1} \Rightarrow r_z = r_1(Z)^{\frac{-2}{m-1}}$$

For Ne-like ions, m=7,

when Z=2, $r_2=0.794r_1$

$$r_{O^{2-}} = 0.794\times 1.76 = 1.40A$$

$$r_{Mg^{2+}} = 0.794\times 0.82 = 0.65A$$

9.4.2 Effective ionic radii

- ***Shannon*** and ***Prewitt*** recompiled the cation-anion separation data for over a thousand oxides and fluorides.

- "***Effective***" here means that these data were deduced from experimentally determined values and the sum of the ionic radii is the most consistent with the measured separation between ions.

The Database is continuously updated!

9.4.3. The trend of variation of ionic radii

1. In each of the groups IA, IIA, IIIA-VIIA in the periodic table, the ionic radius of the elements in the same group increases with the atomic number.

Li^+	Na^+	K^+	Rb^+	Cs^+
0.76	**1.02**	**1.38**	**1.52**	**1.67**

2. Within the same period of the periodic table, the ionic radius of the isoelectronic cations decreases as the positive charge increases.

Na^+ **1.02** Mg^{2+} **0.72** Al^{3+} **0.535**

Au^+ **1.37** Hg^{2+} **1.02** Tl^{3+} **0.885** Pb^{4+} **0.775**

3. The ionic radii of the various valence states of a particular ion vary proportionally to the number of electrons present.

Cr^{2+} **0.80** Cr^{3+} **0.62** Cr^{4+} **0.55** Cr^{6+} **0.44**

4. For an isoelectronic pair of anions, the radius increases slightly as the negative charge increases.

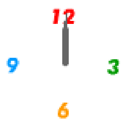
F^-	**1.33**	**O^{2-}**	**1.40**
Cl^-	**1.81**	**S^{2-}**	**1.84**
Br^-	**1.96**	**Se^{2-}**	**1.98**

5. “***Lanthanide contraction***” effect: The six-coordinate trivalent ionic radii of the lanthanides decreases with increasing atomic number from **1.032 Å of La^{3+} to 0.861 Å of Lu^{3+}.**

6. For cations in diagonal position (top-left to bottom-right) of the periodic table, the radii are similar. E.g.,

Li^+ 0.60, Mg^{2+} 0.65;

Na^+ 0.95, Ca^{2+} 0.99; Sc^{3+} 0.81, Zr^{4+} 0.80



9.4.3 Polarization of ions

1. The polarization of a molecule in an external electric field is measured by the induced dipole moment:

$$\bar{\mu} = \mu_E - \mu_0 = \alpha F$$

α: polarizability, **F: strength of electric field**.

2. Ions in an ionic crystal are also polarized by the crystal field.

→ Stronger crystal field induces enhanced polarization of a given ion.

3. Some trends regarding ionic polarization:

- The larger the ionic radius, the higher polarizability the ion has. **$I^- > Br^- > Cl^- > F^-$**, trication: **$La^{3+} > Y^{3+} > Sc^{3+}$**
- Generally anions have larger polarizability than cations.

  e.g. **$F^- >> Na^+$**
- The higher formal charge of a cation, the lower polarizability it has, e.g., **$Ca^{2+} < K^+$**
- The higher formal charge of an anion, the larger polarizability it has, e.g., **$O^{2-} > F^-$**

4. Effects of ion polarization: **ionic bond → covalent bond**.

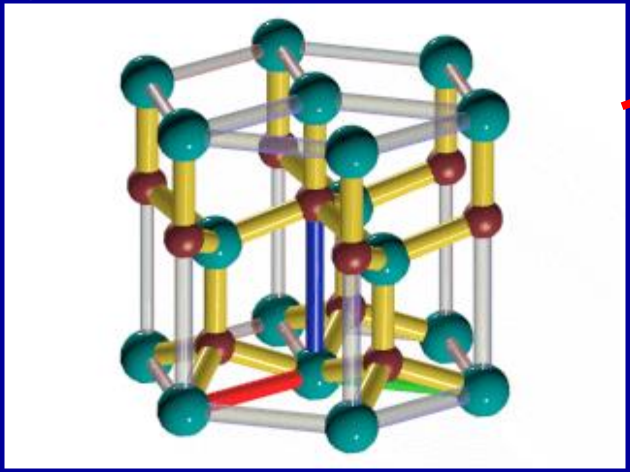
9.5 The Pauling rule of Coordination polyhedra for ionic crystals

1. The nature of coordination polyhedra

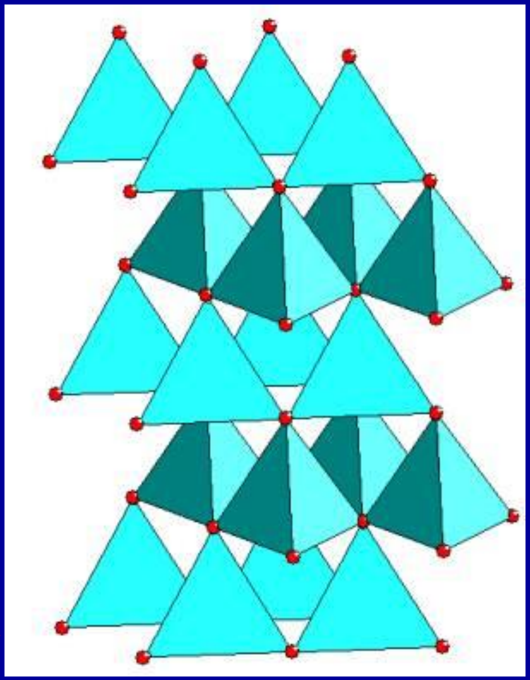
- In ionic crystals, each cation is surrounded by anions, forming a coordination polyhedron.

- The nearest cation-anion distance is the summation of ionic radii.

- The coordination number of the cation is determined by the radius ratio ***R_+/R_-***.



(Wurtzite/纤锌矿)



ZnO

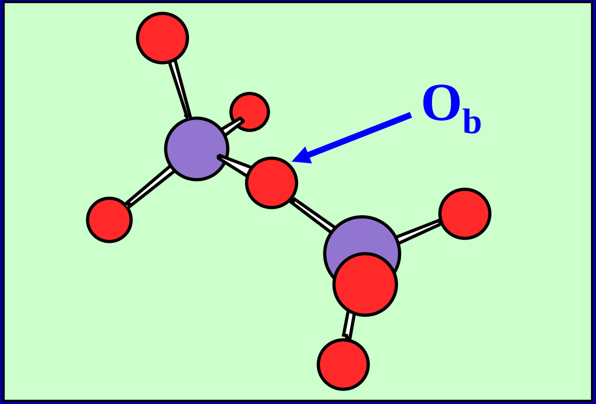
Hexagonal , Zn^{2+} : tetrahedral coordination

2. The electrostatic valence rule

The charge of each anion is equal or close to the sum of the strengths of the electrostatic bonds to it from the adjacent cations.

$$\text{Cation}: \; S_i = Z_i^+/CN_i^+; \qquad \text{Anion}: \; Z^- = \sum_i S_i$$

e.g., Stability of bridging O in



$Si_2O_7^{6-}$ $Z^- = 4/4 + 4/4 = 2$ (stable)

$S_2O_7^{2-}$ $Z^- = 6/4 + 6/4 = 3$ (unstable)

CO_3^{2-} $S_i = 4/3$ ~<< 2

→ The O atom can not bond to another C atom.

→ Being Isolated group

•So do PO_4^{3-}, SO_4^{2-} etc.

SiO_4^{4-} $S_i = 1 << 2$

→ Non-isolated group

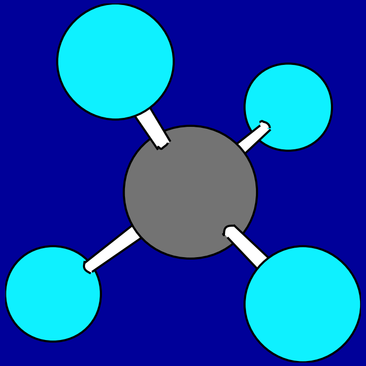
→ The O atom should bond to another Si atom.

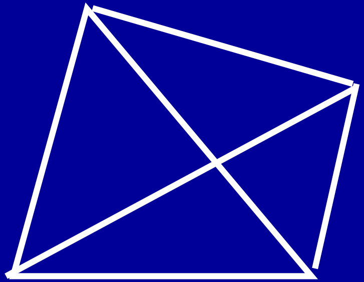
→ Silicates!

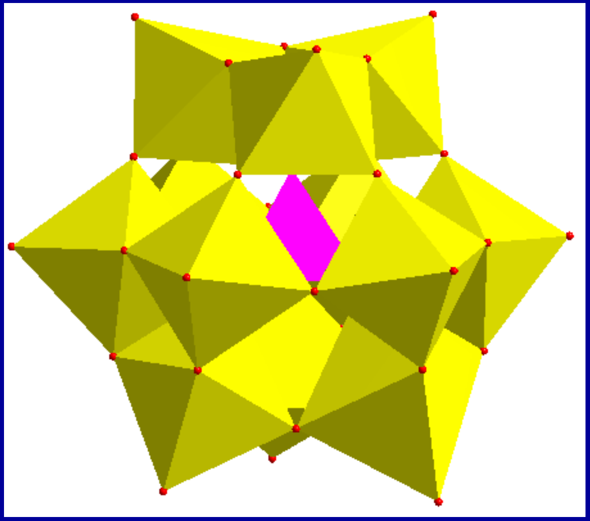
3. The rule of vertex-, edge- and face-sharing

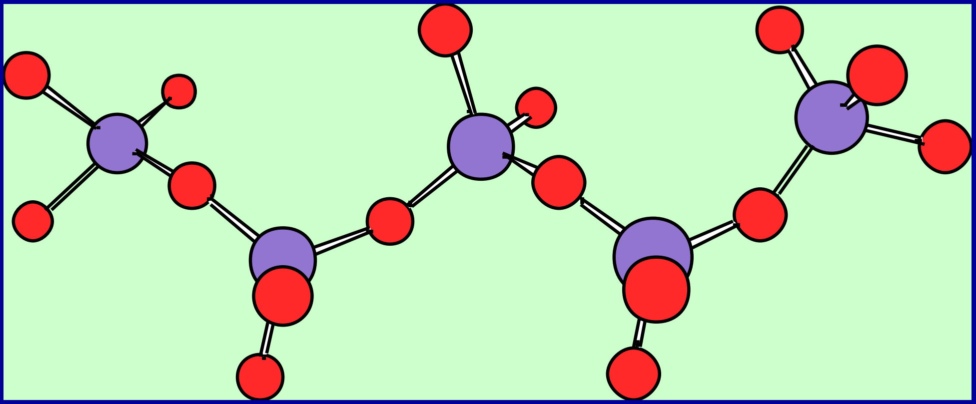
- The presence of shared edges and especially of shared faces in a coordinated structure introduces larger cation-cation repulsion and, as a result, decreases its stability.

- Thus, vertex-sharing of coordination polyhedra is preferred!



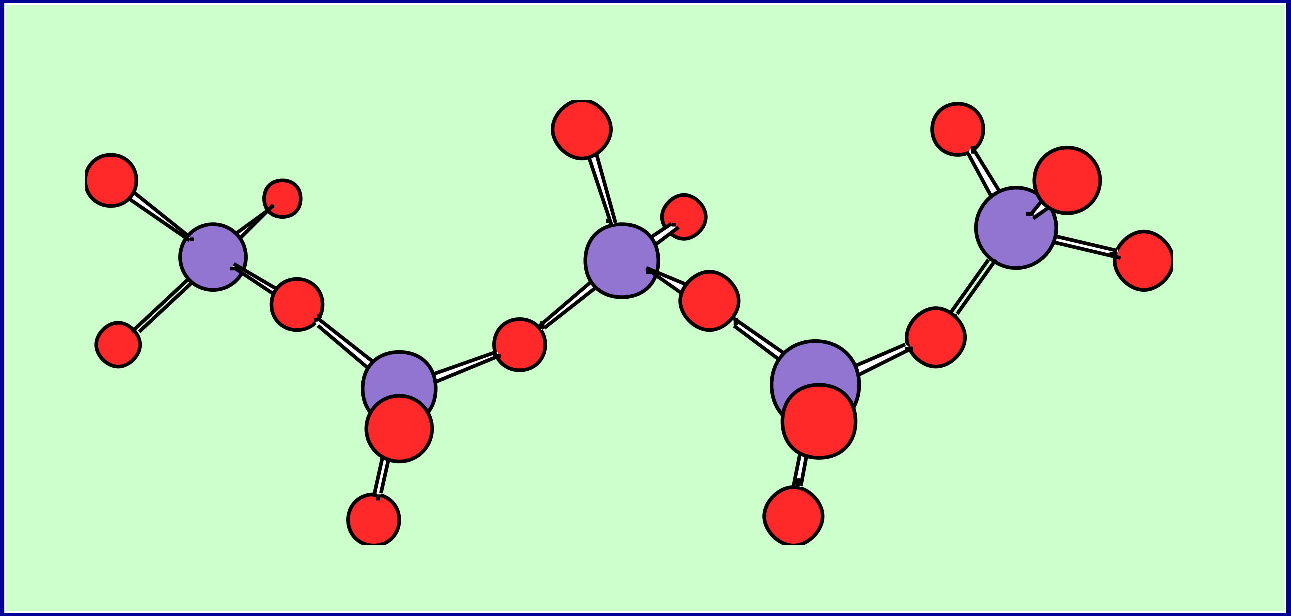


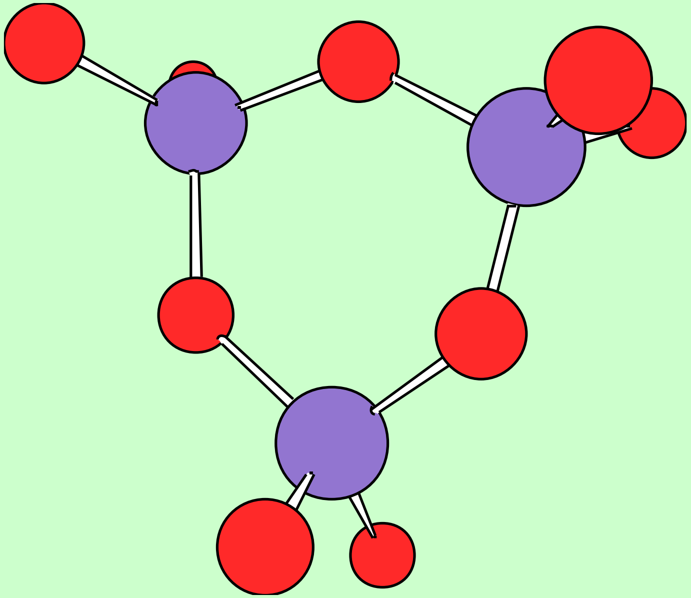




9.6 Structural chemistry of silicates

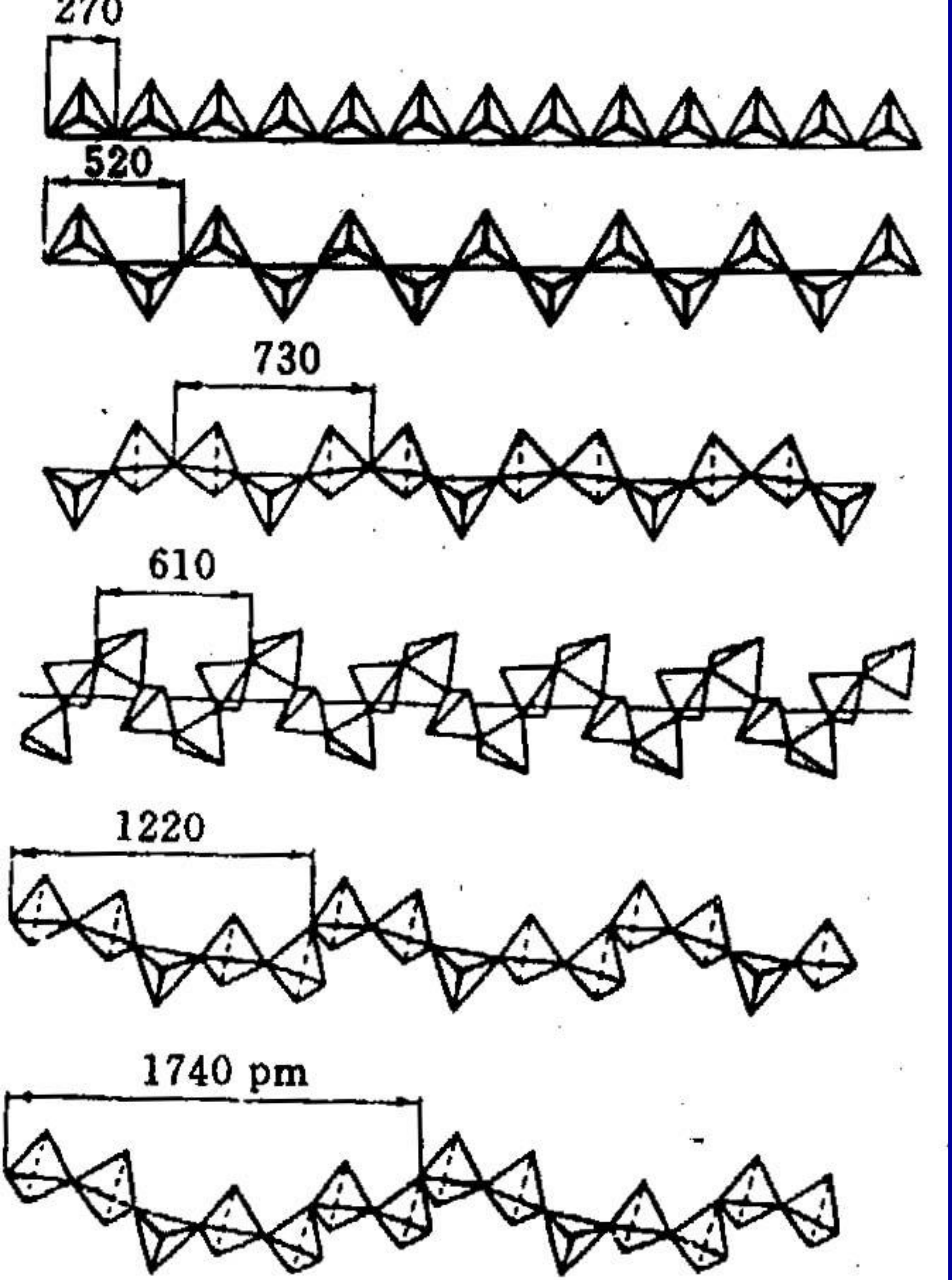
1. Discrete silicates consisting of several SiO_4 coordination-tetrahedra

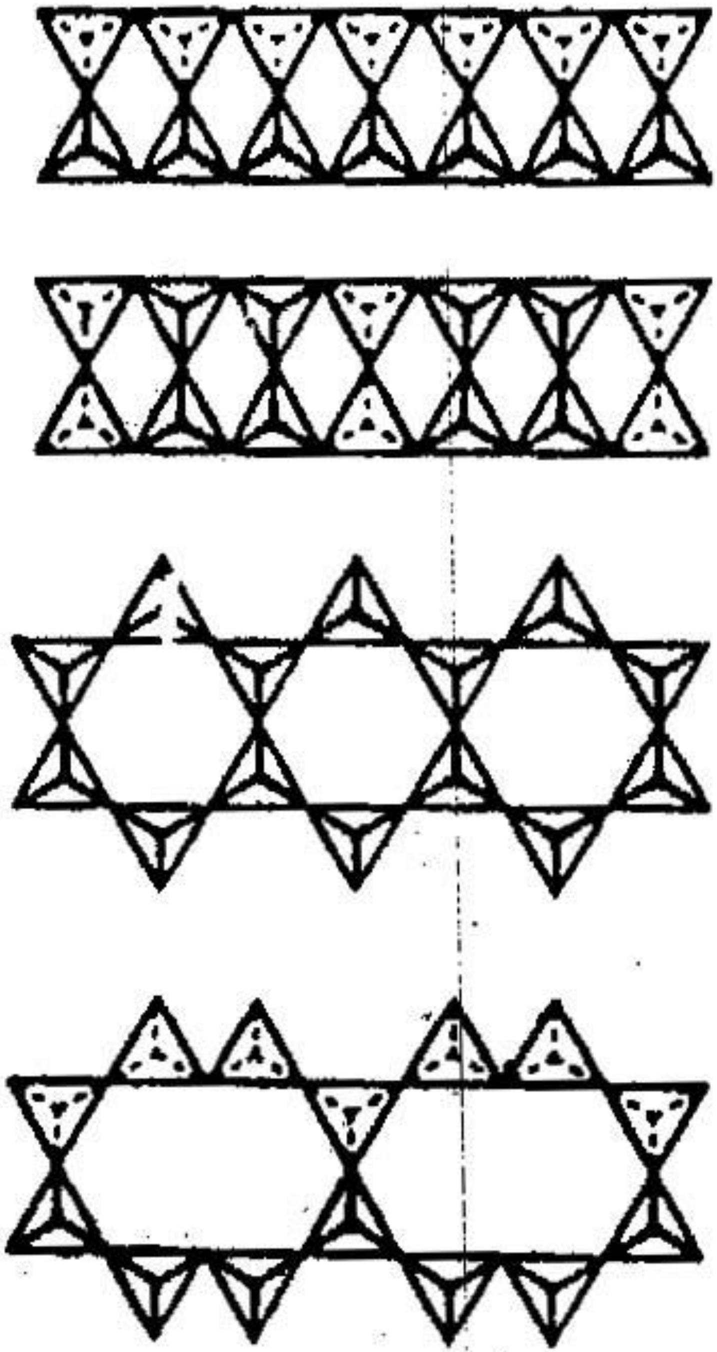




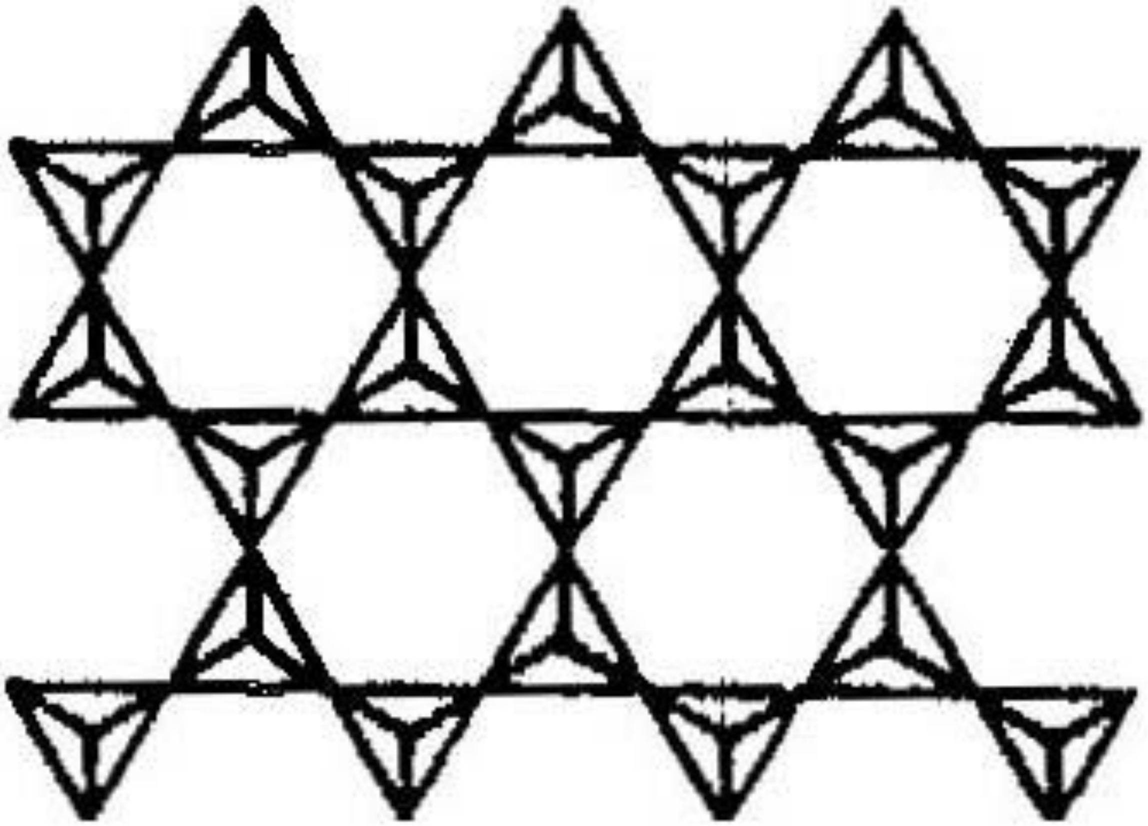
2. Infinite chain silicates

1D cases



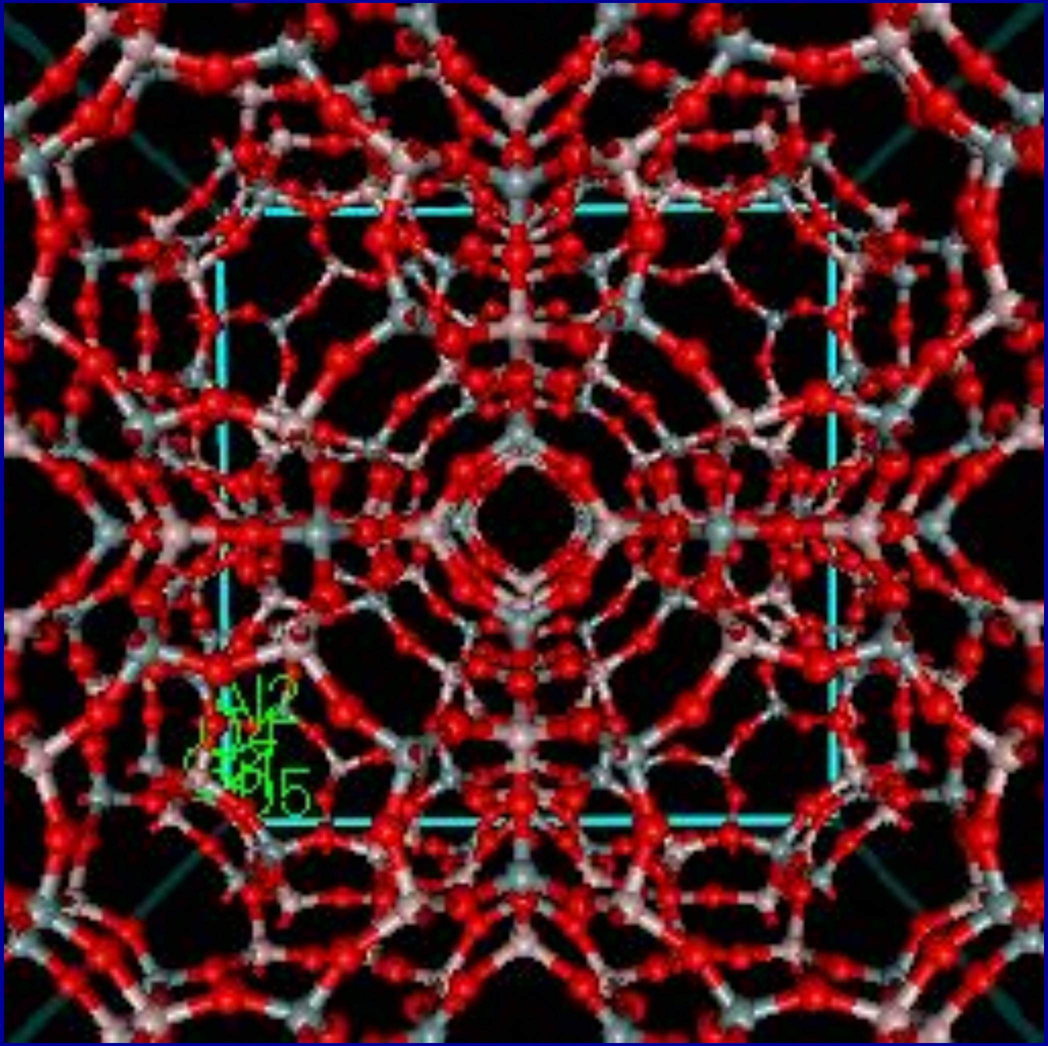


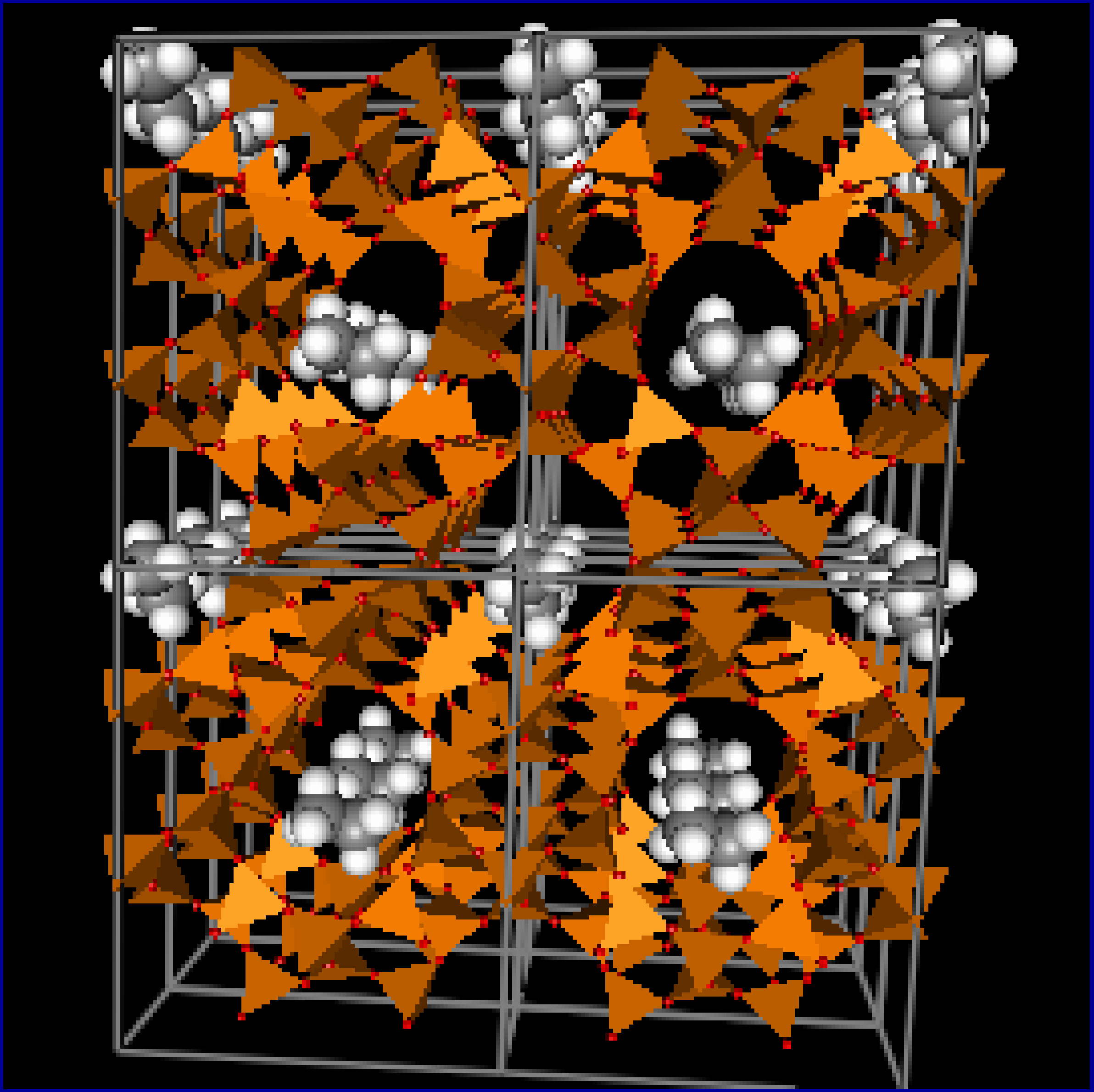
3. Sheet silicates

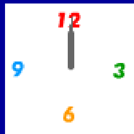


3. Three-dimensional network silicates

A-type
Zeolite





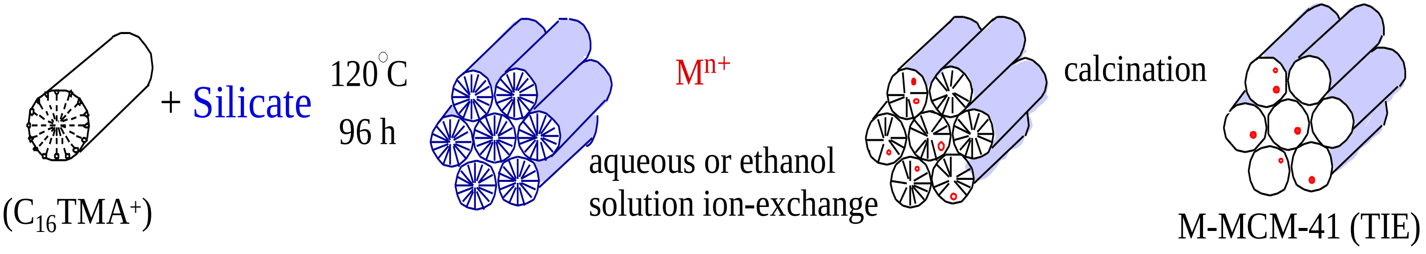

12
9
3
6

Meso-porous compounds

Syntheses

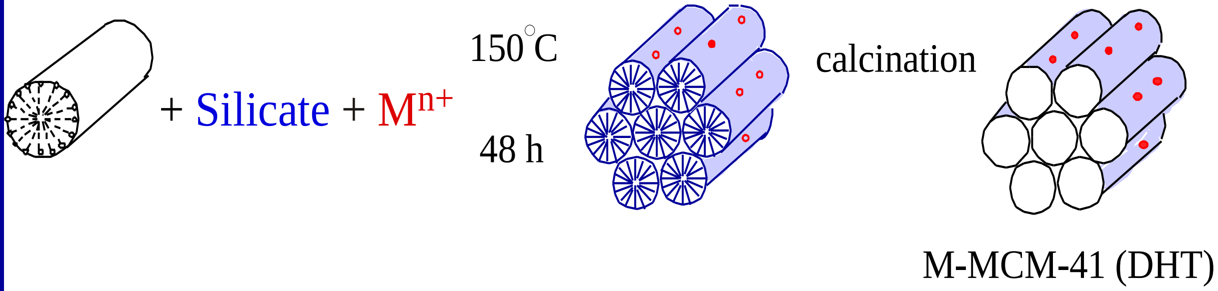
● **M-MCM-41**

Template-ion exchange method



($C_{16}TMA^+$) + Silicate 120°C 96 h M^{n+} aqueous or ethanol solution ion-exchange calcination M-MCM-41 (TIE)

Direct hydrothermal synthesis method



+ Silicate + M^{n+} 150°C 48 h calcination M-MCM-41 (DHT)

V, Cr, Mn, Fe, Co, Ni, Cu, Zn

TBV2//3： 7-9章习题及答案纠错

7.27 已知条件需加 λ=154.18 pm

7.18 答案有误，a= 316.6 pm

8.11 答案有误， 4_1 导致(200) 消光， 最小的三个衍射角对应的衍射指标为(111), (220), (311)

9.9 已知条件错误： (2) “立方体空隙”

答案有误： (1) 简单立方点阵， a = 314 pm

期末考试

时间：　2017年1月12日　10:30-12:30

地点：　南强二 502

注意事项：1）　带科学计算器
　　　　　2）　提前10分钟到场

考前答疑：　1月10-11日，嘉锡楼2楼大厅

Happy New Year!