Chapter 9 Structural chemistry of ionic compounds

9.1 The ionic radii ratio and the coordination polyhedra of ions

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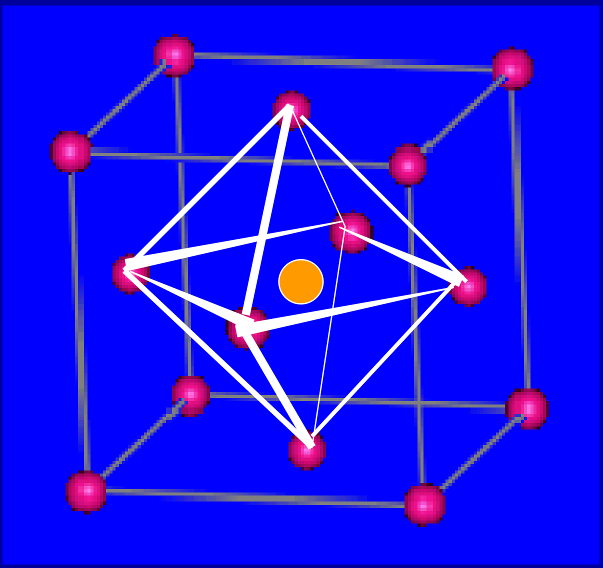
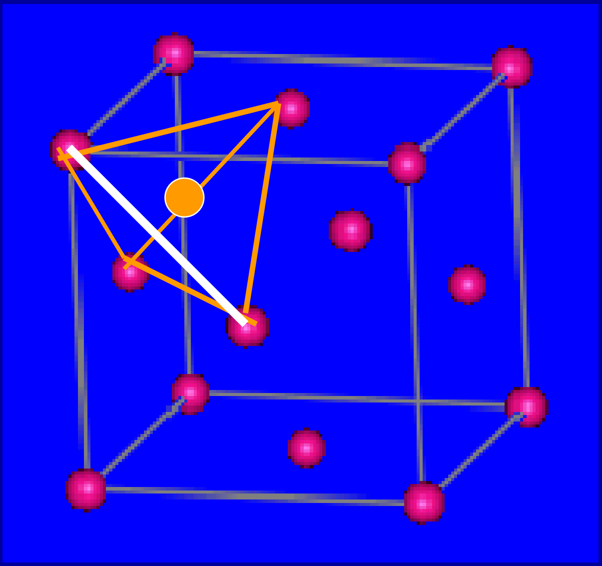
Interstices

octahedral holes



hole size is 0.414R
CN: 6

tetrahedral holes



hole size is 0.225R
CN: 4

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

The rule of the packing of ions

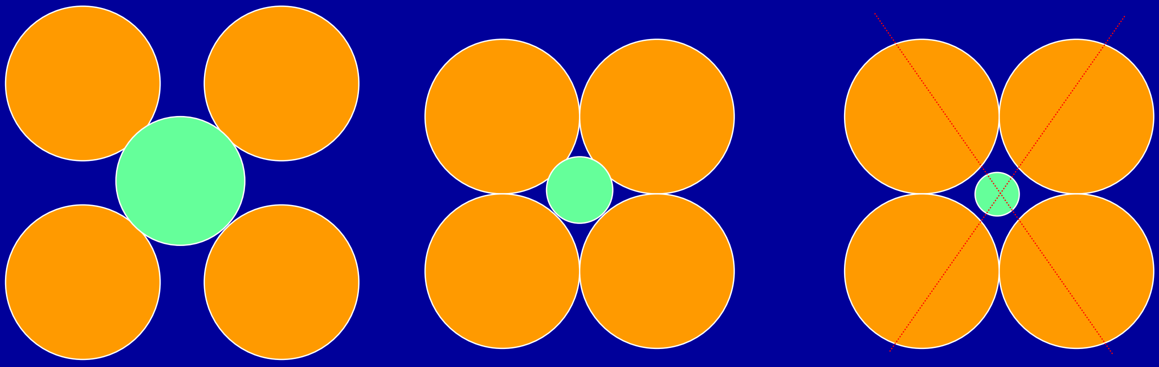


Table 1. The limiting ratio of some coorrdination

Coordination polyhedra	C.N.	minimum r_+/r_-
Triangular	3	0.155
Tetrahedal	4	0.225
Octahedral	6	0.414
Cubic	8	0.732
Cuboctahedron	12	1.000

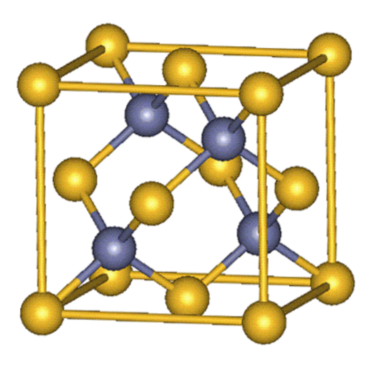
9.2 The crystal structures of Some typical ionic compounds

Answer the following questions:

- The packing style of anions ?
- The position of cations ?
- Crystal System (Bravais Lattice)?
- The C.N. of anion and cation ?
- Atom number in one unit cell?
- Structural formula ?
- Atomic coordinates

ZnS (0.225-0.414) C.N.$^+$:C.N.$^-$ 4:4

(Sphalerite)



Zn:S = 4:4 cubic

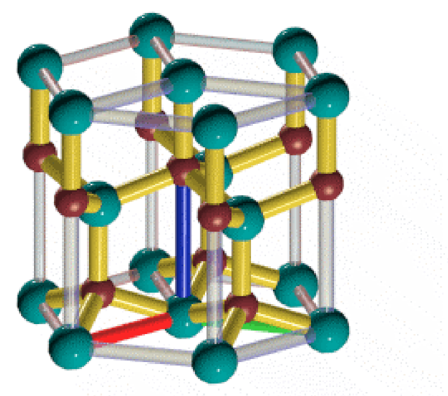
A: 0,0,0; 1/2,1/2,0, 1/2,0,1/2; 0,1/2,1/2

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

• The packing of anions:	fcc
•Bravais Lattice :	Cubic F
•The position of cations:	½ Tetrahedral holes
The C.N. of cation and anion:	4:4
• Atom number in one unit cell:	4:4

ZnS (0.225-0.414)

(Wurtzite)



Zn:S = 2:2 hexagonal

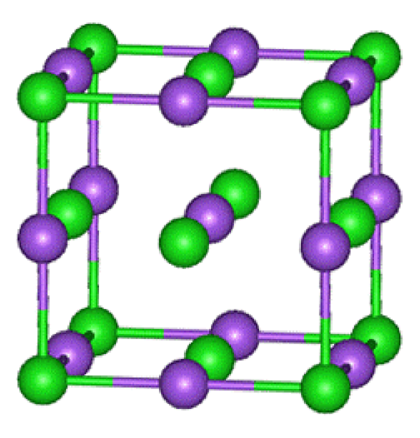
A: 0,0,0, 1/3,2/3,1/2

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

• The packing of anions:	hcp
•Bravais Lattice :	Hexagonal P
•The position of cations:	½ Tetrahedral holes
The C.N. of cation and anion:	4:4
• Atom number in one unit cell:	2:2

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

NaCl (0.732-0.414) Cubic, C.N.$^+$:C.N.$^-$ 6:6,



• The packing of anions:	fcc
•Bravais Lattice :	Cubic F
•The position of cations:	Octahedral holes
The C.N. of cation and anion:	6:6
• Atom number in one unit cell:	4:4

Na:Cl = 4:4

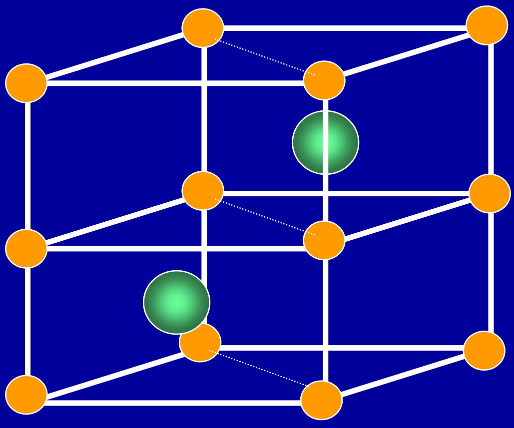
A: 0,0,0; 1/2,1/2,0, 1/2,0,1/2; 0,1/2,1/2

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

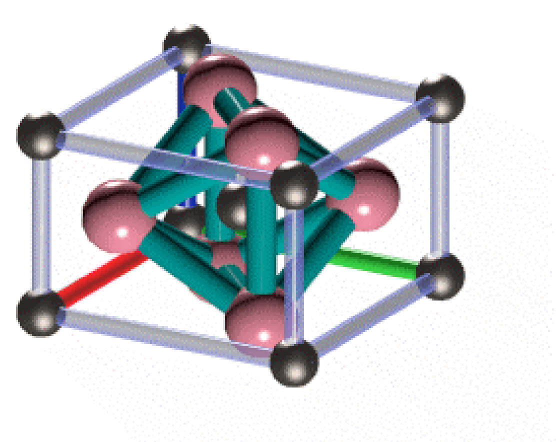
(0.732-0.414) KCl, KBr, SrS, RbI, BaTe, SrSe, CaS, KI, SrTe, MgO, LiF, CaSe, NaBr, CaTe, MgS, NaI, LiCl, (>0.732) KF, SrO, BaO, RbF, RbCl, BaS, CuO, CsF, RbBr, BaSe, NaF, (<0.414) MgSe, LiBr, LiF

NiAs (0.732-0.414) Hexagonal, C.N.$^+$:C.N.$^-$ 6:6,

(0.732-0.414) FeS



TiO$_2$ (Rutile) Tetragonal C.N.$^+$:C.N.$^-$ =6:3



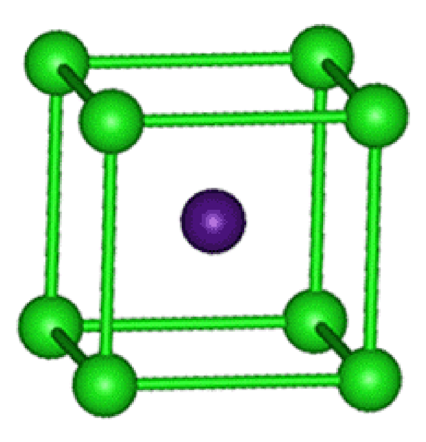
• The packing of anions:	Distorted hcp
•Bravais Lattice :	Tetragonal P
•The position of cations:	½ distorted octahedral holes
The C.N. of cation and anion:	6:3
• Atom number in one unit cell:	Ti:O = 2:4

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

(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$_2$

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



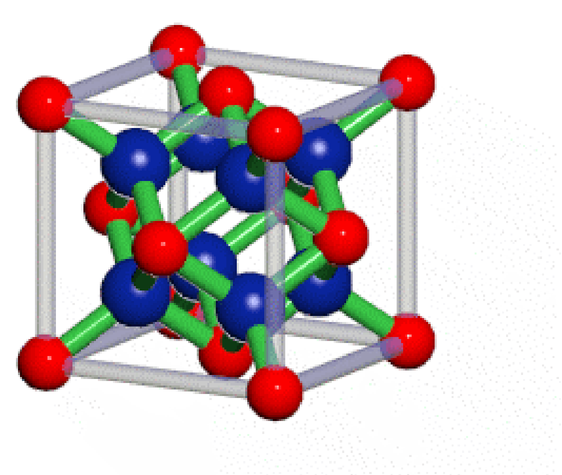
• The packing of anions:	Cubic
•Bravais Lattice :	Cubic P
•The position of cations:	Cubic holes
The C.N. of cation and anion:	8:8
• Atom number in one unit cell:	1:1

A: 0,0,0

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

CsBr, CsI (1-0.732)

CaF_2 (Fluorite) AB_2 type C.N.$^+$:C.N.$^-$ =8:4

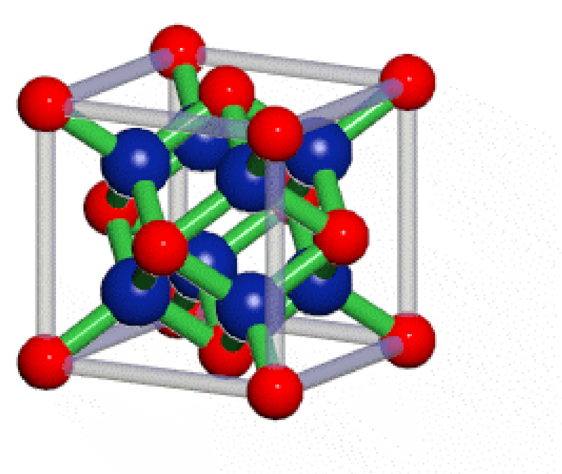


• The packing of anions:	Cubic
•Bravais Lattice :	Cubic F
•The position of cations:	½ Cubic holes
The C.N. of cation and anion:	8:4
• Atom number in one unit cell:	Ca:F = 4:8

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

(>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

Rb2O, Li2O --- anti- Fluorite structure type

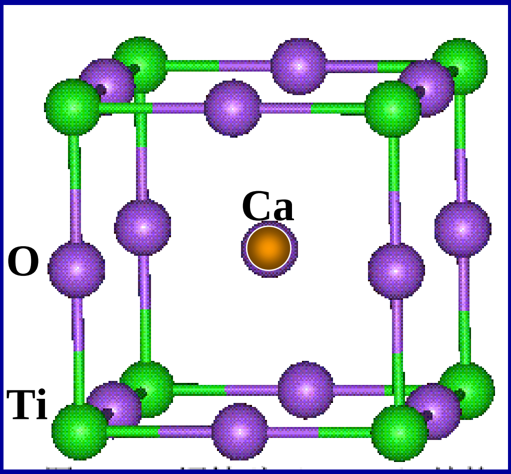


- The packing of anions?
- The position of cations?
- Bravais Lattice ?
- The C.N. of anion and cation?
- Atom number in one unit cell?

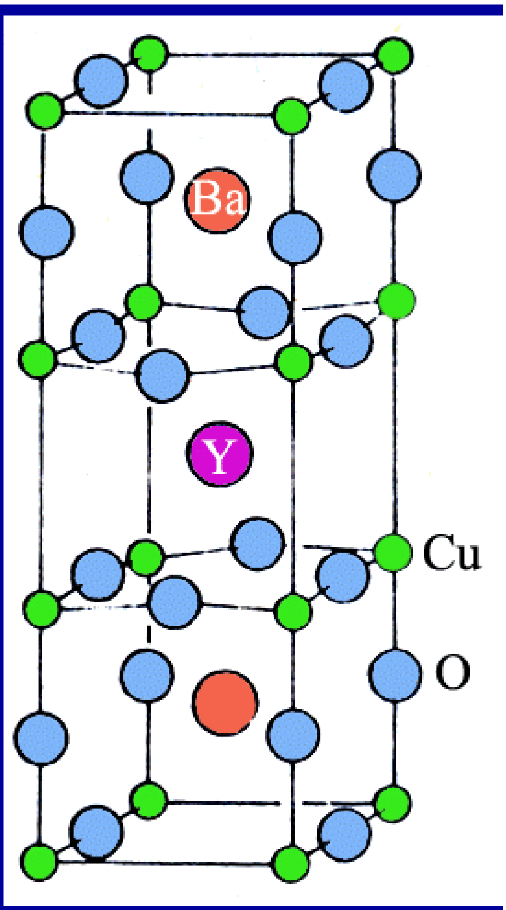
Typical Crystal Structures of Binary Component

Structure Name	Structure Type	Anion Packing	Cation position	Coordination Numbers		Examples
				Cations	Anions	
Soldium Chloride	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 octahedral holes	6	3	TiO_2, MnO_2, SnO_2

$CaTiO_3$ (perovskite) ABX_3



$CaTiO_3$

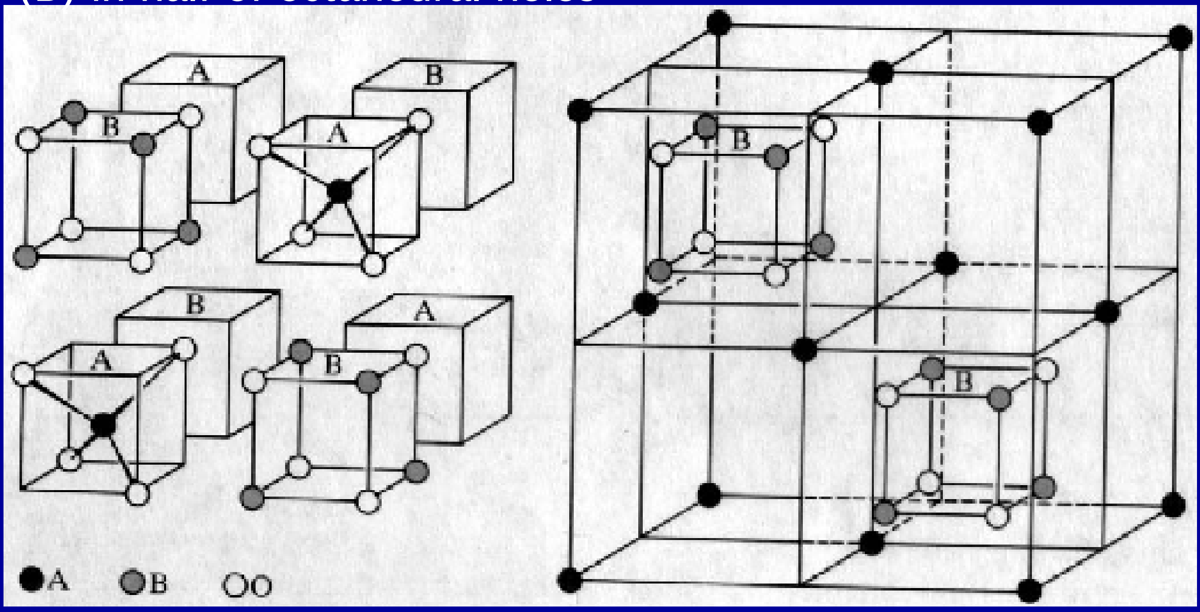


$YBa_2Cu_3O_7$

MgAl$_2$O$_4$ (spinel) AB$_2$X$_4$

O anions form fcc lattice

Mg^{2+}cations (A) in 1/8 tetrahedral holes Al^{3+} cations (B) in half of octahedral holes



eg. FeAl$_2$O$_4$, ZnAl$_2$O$_4$, MgAl$_2$O$_4$

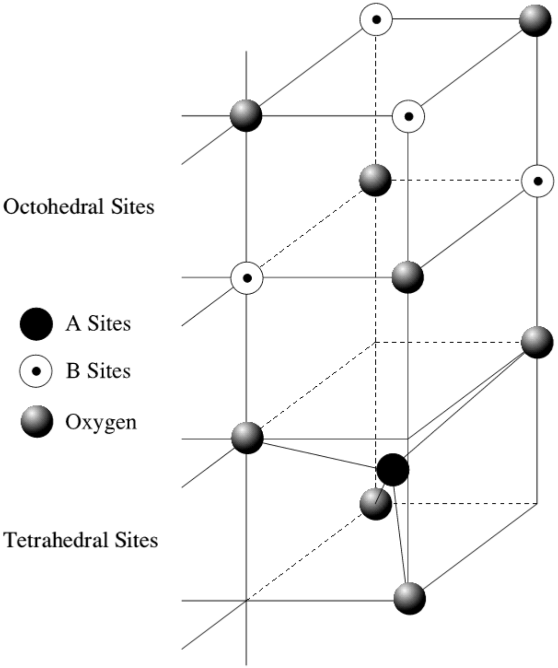
anti-spinel B[AB]O$_4$

magnetite (Fe$_3$O$_4$) = 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^{3+},Fe^{2+}) (A) cations in half of octahedral holes



Spinel $[A]_t[BB]_oO_4$

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

eg. FeFe$_2$O$_4$, FeMgFeO$_4$

Summary of Some Common Crystal Structures

Structure Name	Structure Type	Anion Packing	Cation position	Coordination Numbers Cations	Coordination Numbers Anions	Examples
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	ABX3	FCC(A and X)	All octahedral holes for B	12(A) 6(B)	6	$BaTiO_3$, $SrTiO_3$
Spinel	AB2X4	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

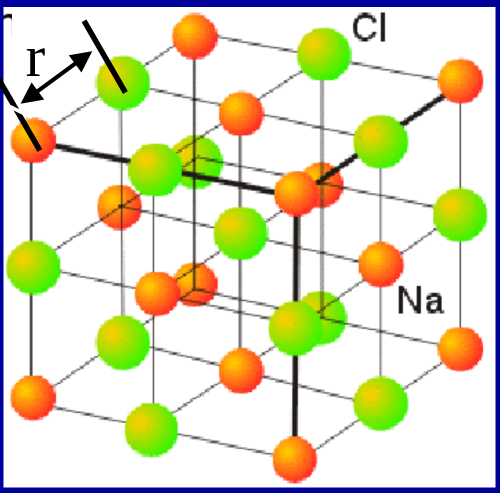
Na+(g) + Cl- (g) ---→ NaCl (s) + U

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

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

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

$A \approx 1.7476$, Madelung constant



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

$A \approx 1.7476$, Madelung constant

Similarly,

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

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

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

$$E_R = Br^{-m}$$

The repulsion energy

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

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

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

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

Lattice energy

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

U = -753kJ/mol

The lattice energy calculated from the Born-Haber cycle

ΔH_f
Na(s) + 1/2 Cl_2(g) -----→ NaCl
| |D Y | U
| S Cl(g)----→Cl^-(g)+Na^+(g)
| I |
Na(g) ------------------------------

Na(s) -→ Na(g) S=+108.4kJ.mol^{-1}

Na(g) -→Na^+(g)+e I=+495.0kJ.mol^{-1}

1/2Cl_2(g) -→Cl(g) D=+119.6kJ.mol^{-1}

Cl(g)+e-→Cl^-(g) Y=-348.3 kJ.mol^{-1}

Na(s) + 1/2 Cl_2(g) -→NaCl ΔH_f=-410.9 kJ.mol^{-1}

ΔH_f = S+I+D+Y+U

U=ΔH_f –(S+I+D+Y)=-785.6 kJ.mol^{-1}

9.4 Ionic radii

9.4.1 The determination of ionic radii

Lande: (1920) The cell parameters for MnS and MgS as well as MgSe and MnSe (NaCl structure type) are nearly identical. Lande suggested that the anions in the structure were contact with one another. Then

r_{s2-}=2.60/√2 =1.84 A

r_{se2-}=2.73/√2 = 1.93 A

Pauling (1927): Pauling deduced many ionic radii from the internuclear separations of five different crystal (NaF, KCl, RbBr, CsI and Li2O) 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 which is dependent on the quantum number n.

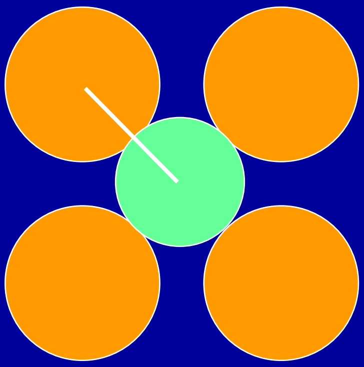
for NaF:

by Slater rule σ=2x0.85 + 8x0.35=4.5

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

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

$r_F- = c_n/(9-4.52)$



From the experimental value of

$r_{Na+} + r_F- = 2.31$

Hence: $r_{Na+} = 0.95A$, $r_F- = 1.36A$, $c_n = 6.15$

From the value of c_n, one can calculate the radii of all univalent Ne-like ions:

$r_O2- = 6.15/(8-4.52) = 1.76\ (1.77)A$

$r_{Mg2+} = 0.82\ A$

$r_O2- + r_{Mg2+} = 2.58\ A \gg 2.10\ A$ (the experimental value)

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

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

$Z^2 r_z^{m-1} = 1^2 r_1^{m-1}$

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

For Ne-like ions, m=7, Z=2 $\quad r_2 = 0.794 r_1$

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

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

9.4.2 Effective ionic radii

Shannon and Prewitt recompiled the cation-anion separation data for over a thousand oxide and fluorides. “Effective” here means that these data were deduced from experimentally determined values and the sum of the ionic radii is most consistent with the measured separation between ions.

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 A of La^{3+} to 0.861A of Lu^{3+}.

6. For cations in diagonal position (top-left to bottom-right) of the periodic table, the radii are similar. (Li^+ 0.60, Mg^{2+} 0.65; Na^+ 0.95, Ca^{2+} 0.99; Sc^{3+} 0.81, Zr^{4+} 0.80)

9.5 The Pauling rule of ionic crystal structure

1. The nature of the coordination polyhedra

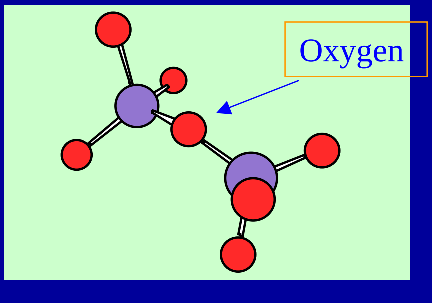
The coordination number of the cation is determined by the radius ratio.

2. The electrostatic valence rule

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

$$Z_{\_} = \sum_i s_i = \sum_i \frac{Z_i}{\nu_i}$$

$Si_2O_7^{6-}$ $Z_-=4/4+4/4=2$ (stable), $S_2O_7^{2-}$ $Z_-=6/4+6/4=3$ (not stable)



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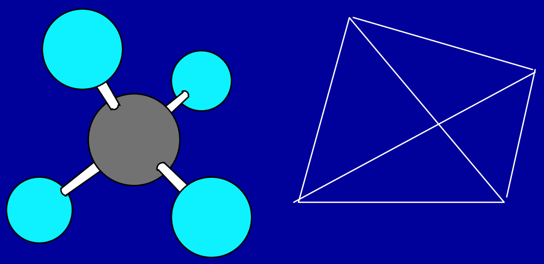
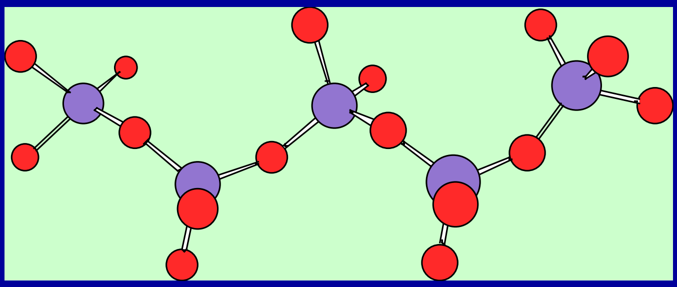
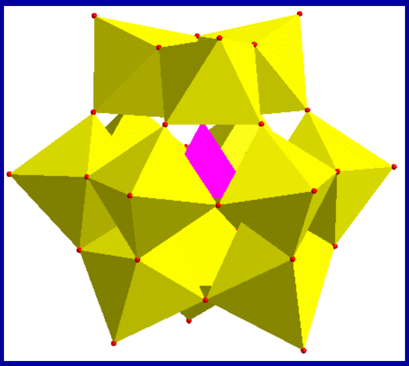
3. The rule of vertex-, edge- and face-sharing

The presence of shared edges and especially of shared faces in a coordinated structure decreases its stability.

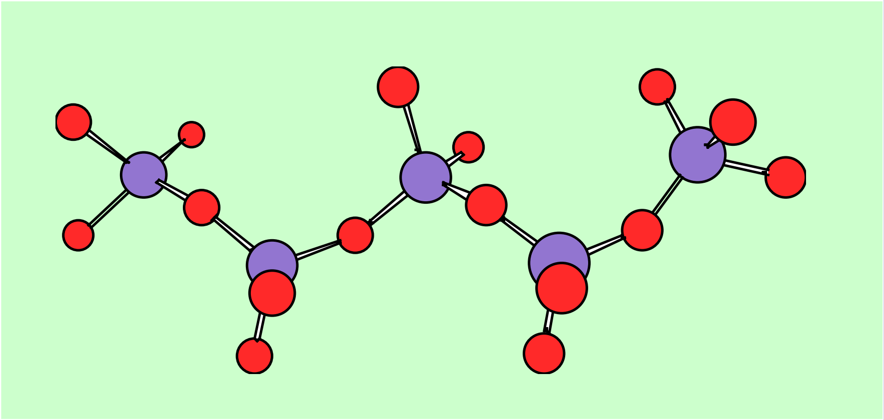


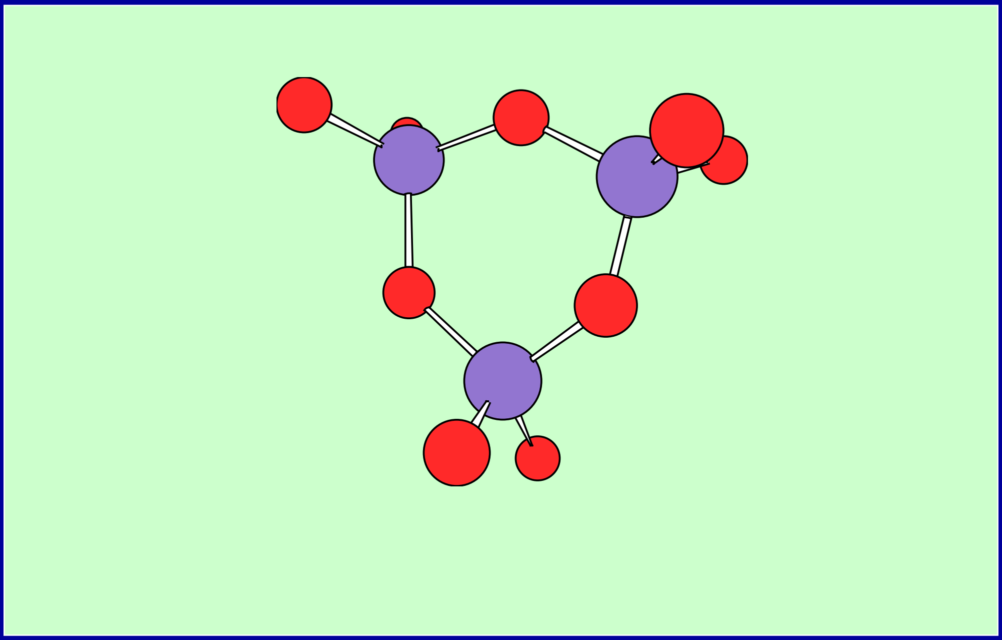




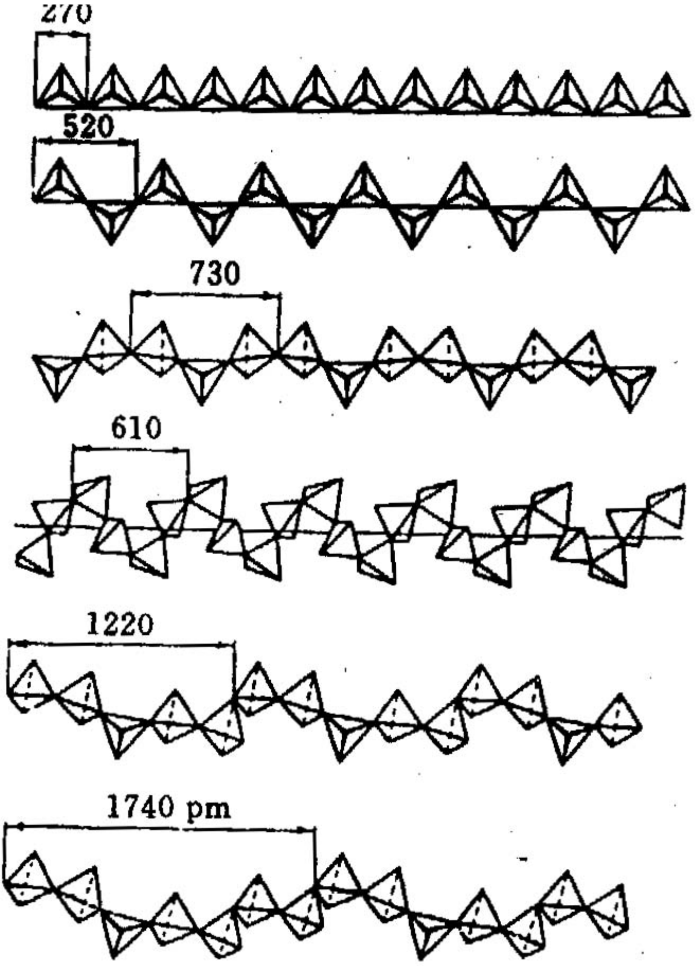
9.6 Structural chemistry of silicates

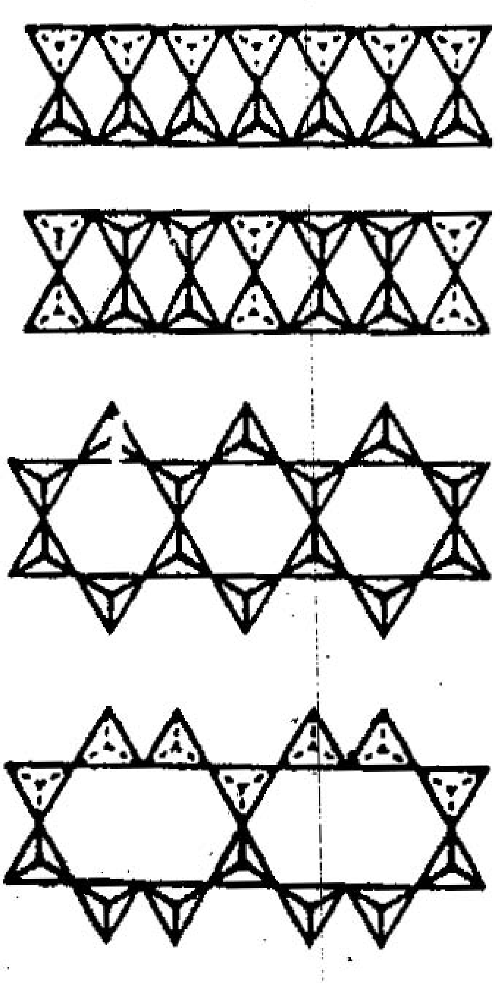
1. Discrete silicates SiO4



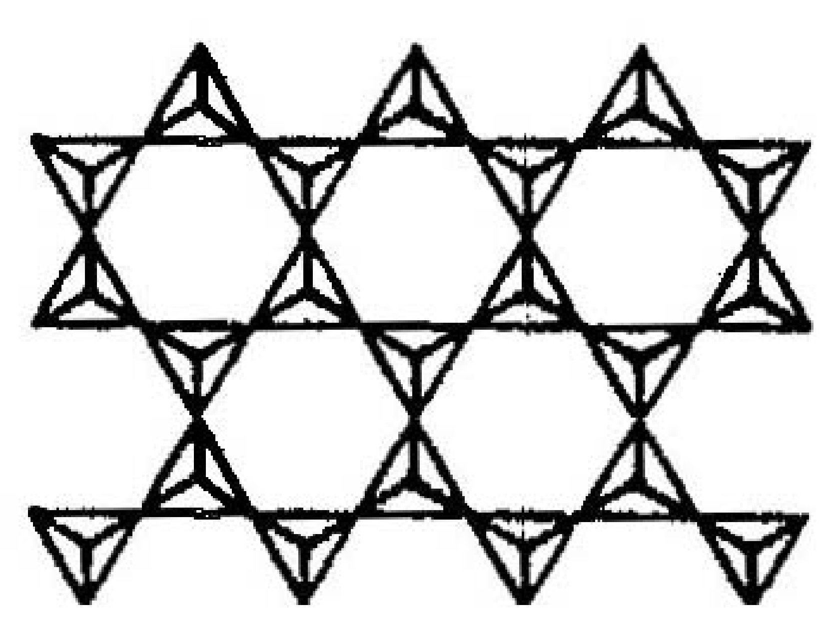


2. Infinite chain silicates





3. Sheet silicates



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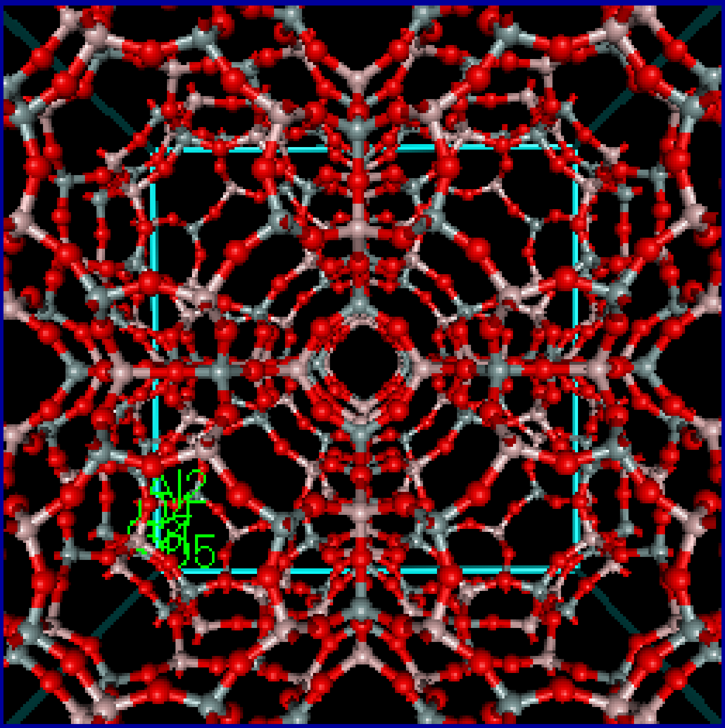
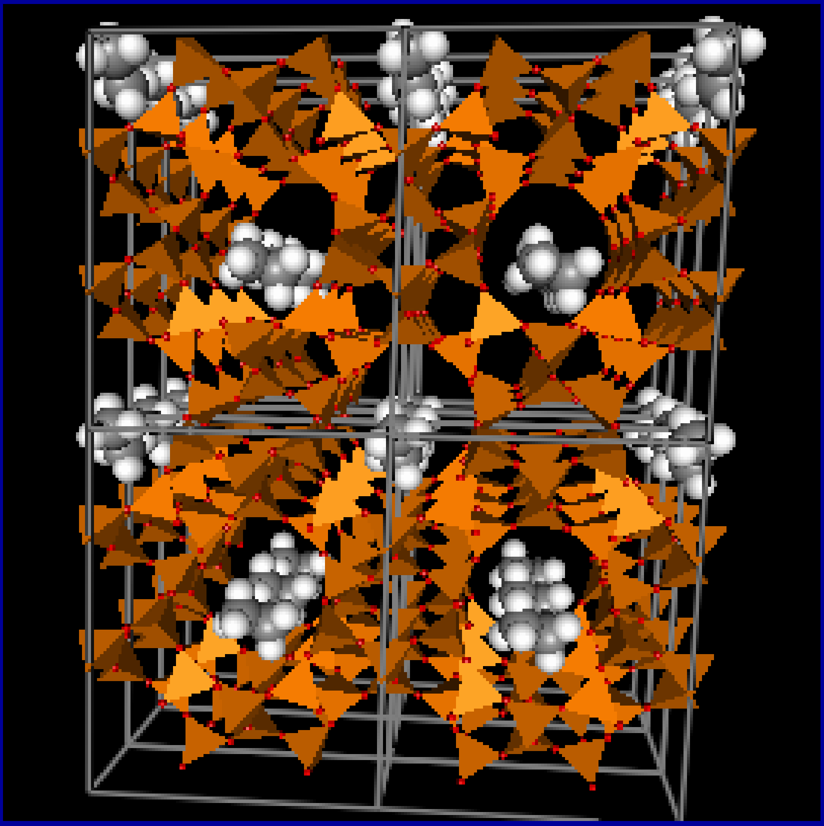
3. Three-dimensional network silicates

A-type
Zeolite



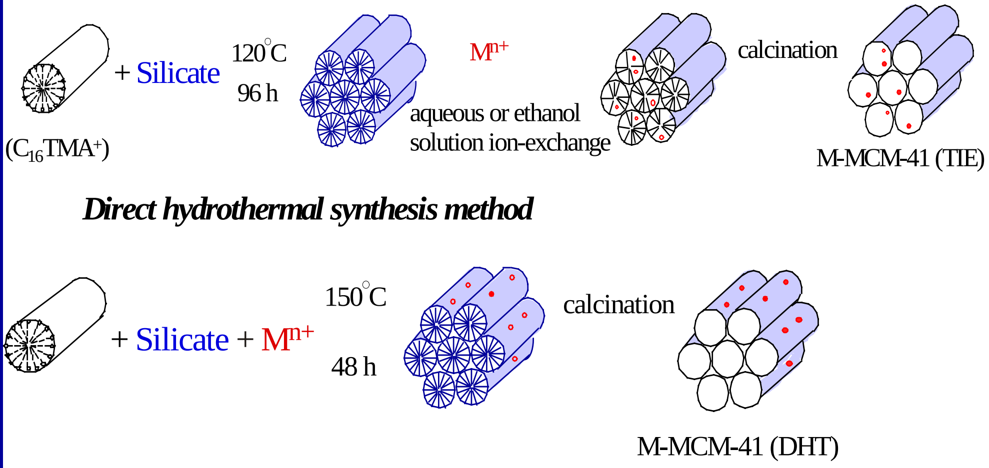


Meso-porous compounds

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

9.7 Crystals of Functional Materials

- High-Temperature Super-conductive Materials ($YBa_2Cu_3O_7$, …)
- Non-linear Optical Crystals (KDP, BBO, …)
- Magnetic Materials
- Piezocrystals
- Optical-electric Materials