CERAMICS, GLASS AND REFRACTORIES

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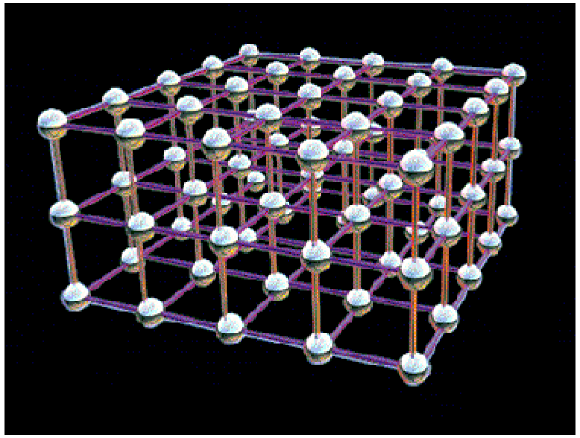
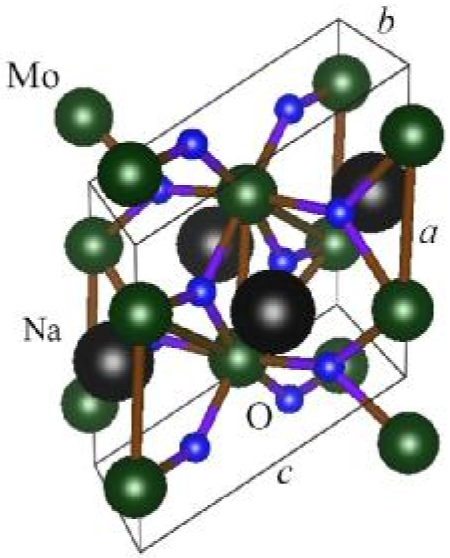
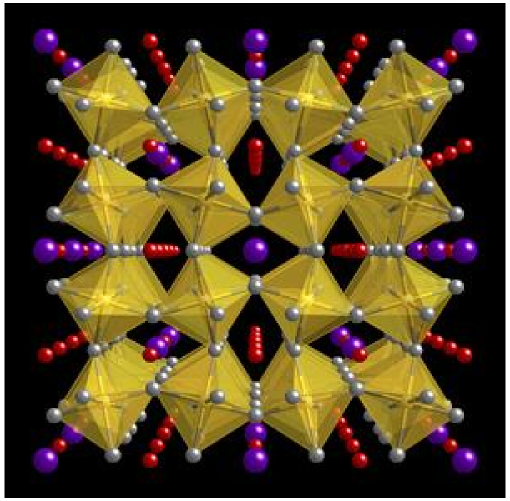
2) Materials Structure







Ceramic Bonds

Pauling: $\% \text{ Ionic character} = 100 \cdot \left\{ 1 - e^{\frac{-(X_A - X_B)^2}{4}} \right\}$

Percentage of ionic and covalent character of the bond for some ceramic materials ⇨ **determines the CRYSTALLINE STRUCTURE**

Ceramic Material	Atoms in bond	$X_A - X_B$	% Ionic Character	% Covalent Character
MgO	Mg—O	2,3	73	27
Al_2O_3	Al—O	2,0	63	37
SiO_2	Si—O	1,7	51	49
Si_3N_4	Si—N	1,2	30	70

Electronegativity X - is a measure of the strength with which an atom in a molecule attracts electrons

Type of bond	*Bond energy (kJ/mol)*
Ionic	50–1000
Covalent	200–1000
Metallic	50–1000
van der Waals	0.1–10
Hydrogen	10–40

The building criteria for the crystal structure are

Maintain neutrality

Charge balance dictates chemical formula

Achieve closest packing

IONIC CERAMICS

Ionic structure : packing of anions with cations in interstitials

The ions tend to pack densely in order to reduce E_{total}

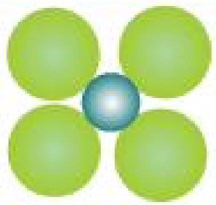
Sizes C^+ A^- ⇨ ($r_{cation} < r_{anion}$)

Electroneutrality

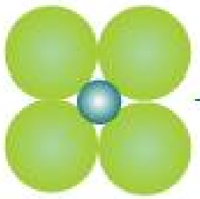
Coordination Index (By increasing C.I ⇨ increase stability)

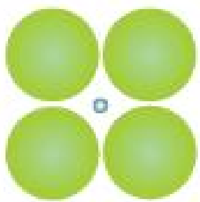
Sharing of polyhedral (sharing vertices instead of edges or faces (increases the distance between cations)

PACKING OF IONS



STABLE





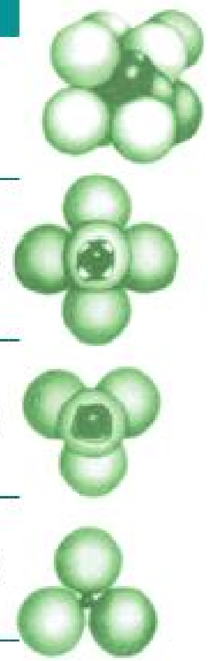
UNSTABLE

➪vibrates in its cage of A^-

The relation between radius when A^- and C^+ are in contact

➪ **Relation of radius is critical** (*minimum*)

Arrangement of A^- around C^+ central and C.I.	Cation/anion Radius ratio r_C/r_A
C.I. 8 Corners of a cube	0.732-1.0
C.I 6 Corners of an octahedron	0.414-0.732
C.I 4 Corners of a tetrahedron	0.225-0.414
C.I. 3 Corners of a triangle	0.155-0.225



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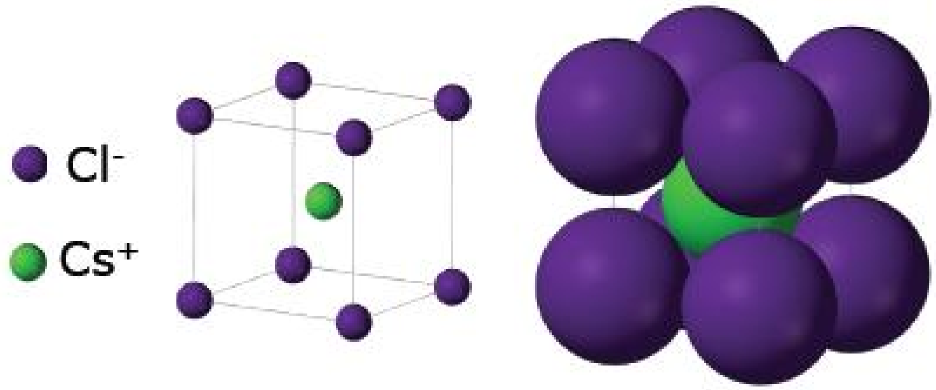
SIMPLE CUBIC STRUCTURE: CsCl

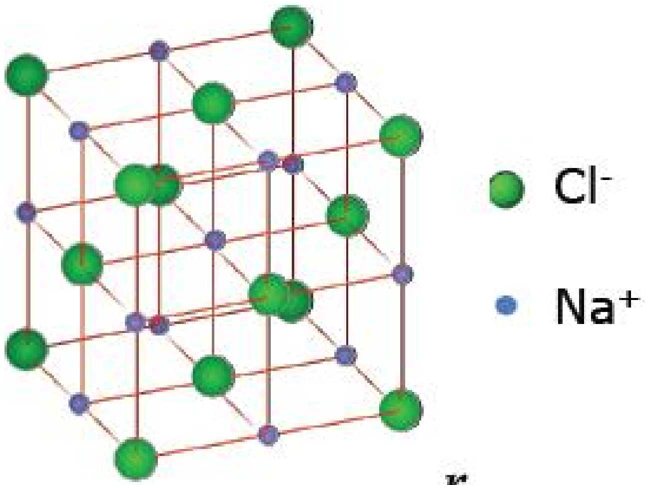


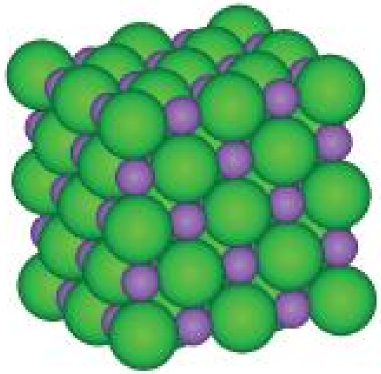
- Cl^- : cubic
- Cs^+: centre of the cube
- C.I.: 8

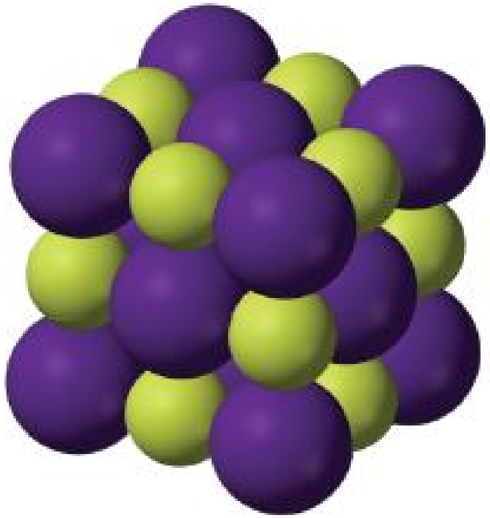
$$\frac{r_{Cs^+}}{r_{Cl^-}} = 0,94 > 0,732 \Rightarrow C.I. = 8 \Rightarrow \text{Cubic structure}$$

Ceramics that have this type of structure: **CsBr, TlCl, TlBr.**

FCC STRUCTURE: NaCl





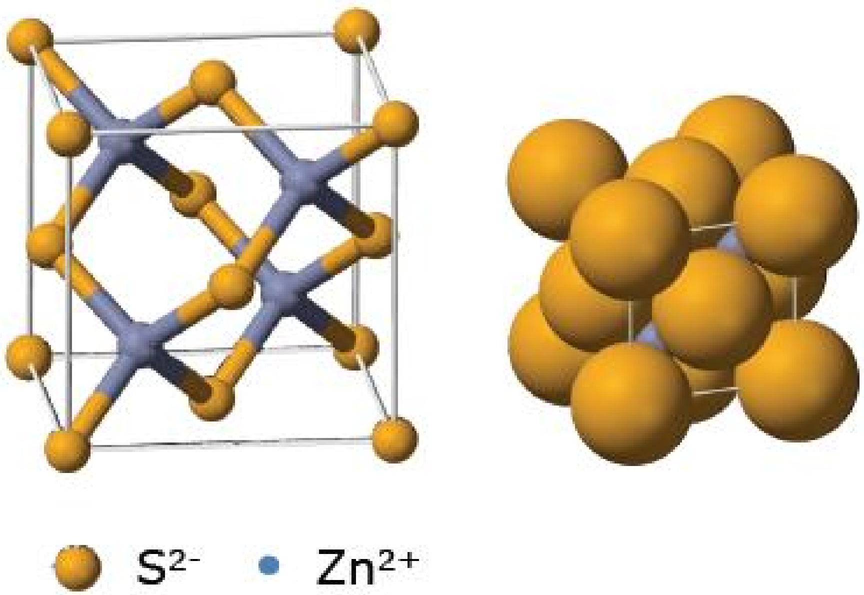


$$\frac{r_{Na^+}}{r_{Cl^-}} = 0{,}56 > 0{,}414 \Rightarrow C.I. = 6 \Rightarrow \text{Octahedral coord.}$$

- Cl^-: FCC packing
- Na: all octahedral interstitials.
- 4 Na^+ and 4 Cl^- per unit cell C.I.=6

Ceramics that have this type of structure: **MgO, CaO, FeO, NiO**

FCC STRUCTURE: Zn Blende-ZnS



- S^{2-}: FCC packing
- Zn^{2+}: ½ tetrahedral interstitials
- 4 Zn^{2+} and 4 S^{2-} per unit cell

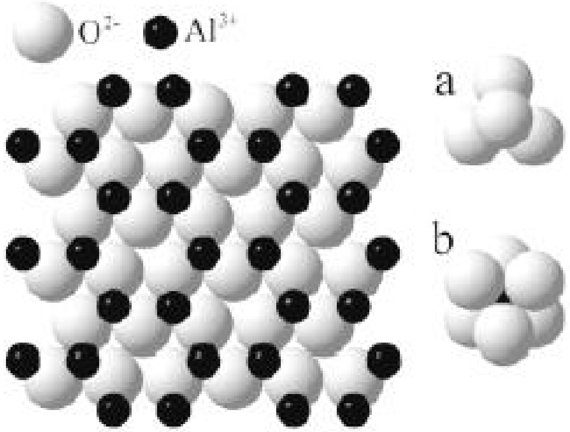
$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.345 \Rightarrow C.I. = 4$$

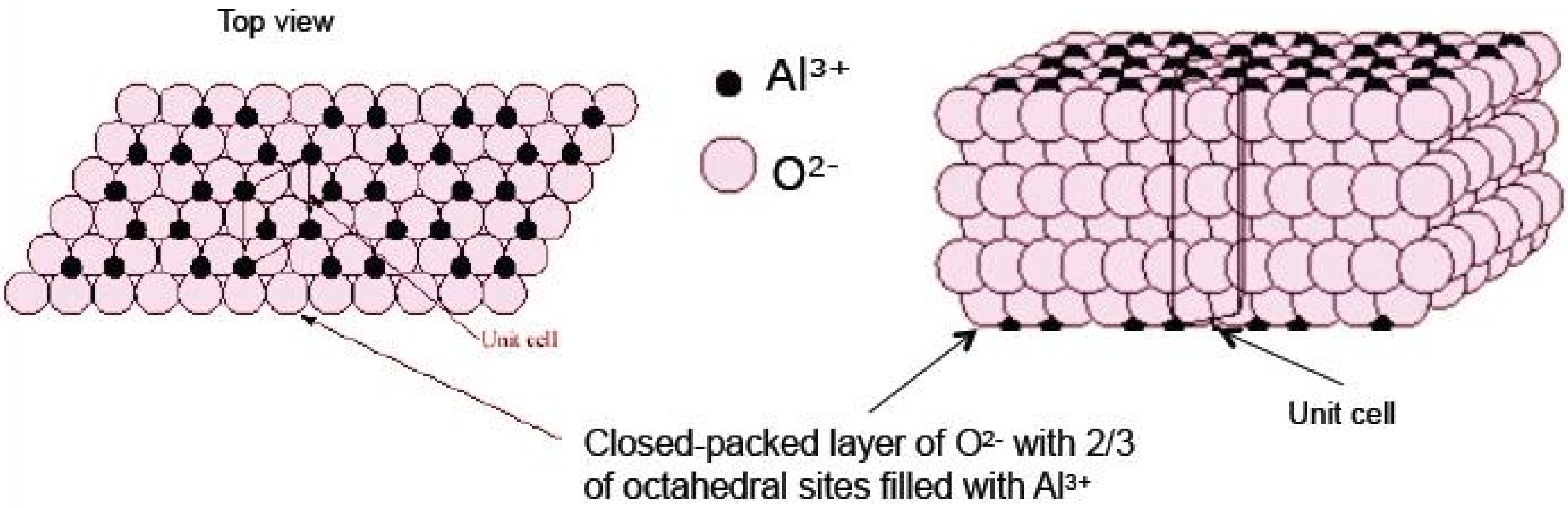
According to Pauling bond **Zn-S ~87% covalent**

Ceramics that have this type of structure: Typical semiconductors **: CdS, HgTe, NiAs, SiC, GaAs**

HCP STRUCTURE: CORUNDUM (ALUMINA)

- O^{2-}: HCP packing → 6 ions
- Al^{3+}: 2/3 octahedral interstitials → 4 ions
- I.C.(Al^{3+}): 6 ; I.C.(O^{2-}): 6

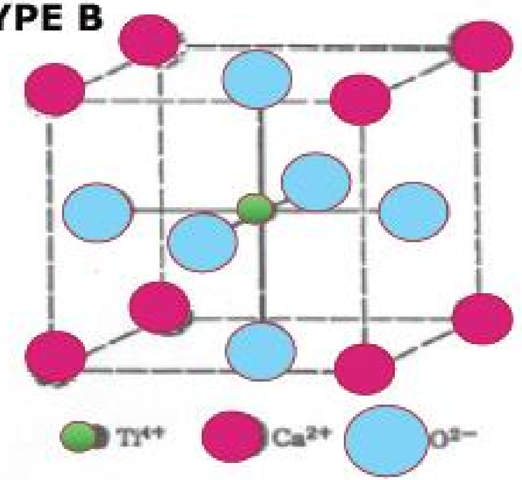


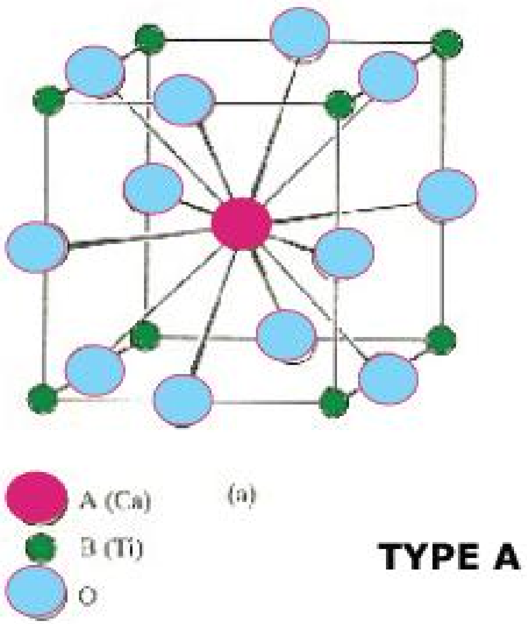


Ceramics that have this type of structure: Cr_2O_3, Fe_2O_3, Al_2O_3 ...

CRYSTALLINE STRUCTURE OF PEROVSKITE ABO_3

TYPE B





TYPE A

A and B cations with different size ($r_A >>> r_B$)

- O^{2-} and Ca^{2+}: **fcc** packing
- Ti^{4+}: **1/4 octahedral sites**
- C.I.(Ti^{2+}): 6 ; C.I.(Ca^{2+}): 12

Ceramics that adopt this type structure:

$BaTiO_3$, $CaTiO_3$, $SrTiO_3$, $PbZrO_3$, $KNbO_3$, $LiNbO_3$,...

Ferroelectric Materials,

Magnetic Superconductor properties ($YBa_2Cu_3O_7$)

Summary of Some Common Ceramic Crystal Structures

Structure name	Structure type	Anion packing	Coordination numbers		Examples
			cation	anion	
Rock salt (sodium chloride)	AX	FCC	6	6	NCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8	8	CsCl
Zinc Blende (sphalerite)	AX	FCC	4	4	ZnS, SiC
Fluorite	AX_2	Simple cubic	8	4	CaF_2, UO_2 ThO_2
Perovskite	ABX_3	FCC	12 (A) 6(B)	6	$BaTiO_3$, $SrZrO_3$, $SrSnO_3$
Spinel	AB_2X_4	FCC	4(A) 6(B)	4	$MgAl_2O_4$, $FeAl_2O_4$

COVALENT CERAMICS

They are structural ceramics

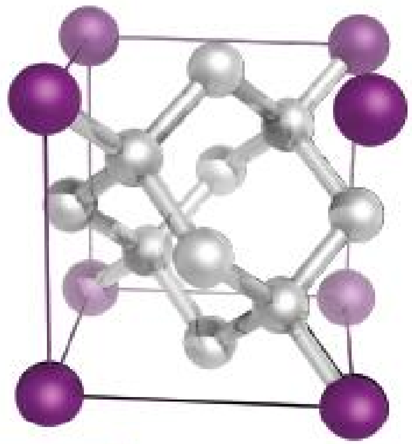
DIAMOND → Structure type blend

C→ sp^3 → c.i. 4 → Tetrahedral CC_4. Bond 100% covalent.

- ↑ wear resistance
- ↑ tensile strength

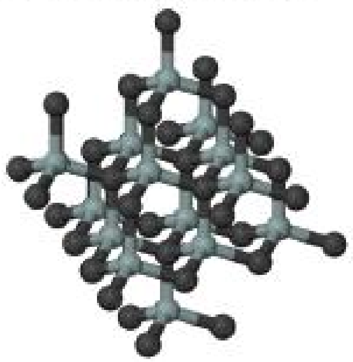
↑ **hardness**

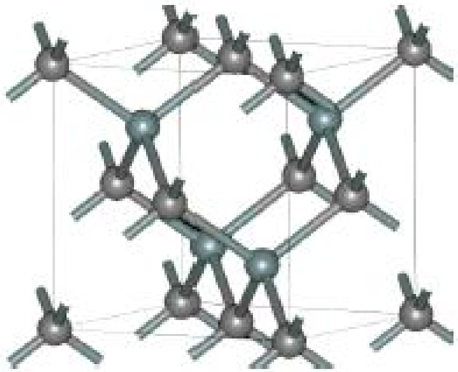
Insulator



SiC → Diamond type structure (spherullite)

- Applications: Good abrasive properties. 89% covalent bond
- High hardness, chemically inert.





COVALENT CERAMICS

They are structural ceramics

Si_3N_4 → Cutting Elements, blades, rotors

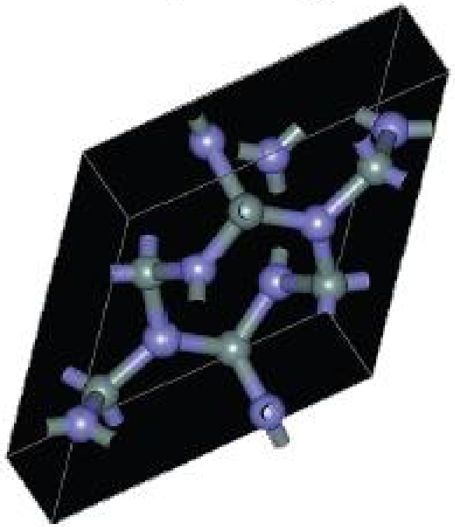
Si → sp³ → c.i. 4 → SiN_4 Tetrahedra

N → sp² → c.i. 3 → N coordinated to 3 Si

Open structure.

70% covalent bond

β-SiN_4



Sialons $Si_{6-z}Al_zO_zN_{8-z}$(1971)

It is a solid solution between nitrides and oxides. Derived from Si_3N_4, by substituting z atoms of Si for Al atoms. In order to compensate the valence difference, the same number of N atoms are substituted by O. Cutting tools, antifriction rollers, motors components.

STRUCTURE OF SILICATES

Si and O are the most abundant elements in the earth's crust

They are the base of traditional ceramics

Useful engineering materials because →

- Low price
- Great availability
- Special properties

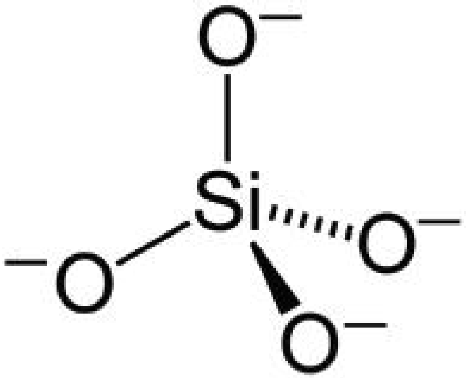
	Composition (wt%)					
Ceramic	SiO_2	Al_2O_3	K_2O	MgO	CaO	Other
Silica refractory	96					4
Fireclay refractory	50-70	45-25				5
Mullite refractory	28	72				-
Electrical porcelain	61	32	6			1
Steatite porcelain	64	5		30		1
Portland cement	25	9			64	2

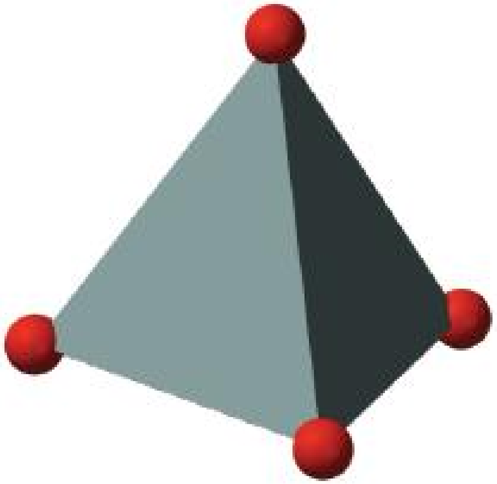
Composition of some silicate ceramics

Fundamentally in:

- Construction (bricks, cement, glass)
- Electrical and thermal insulating materials

STRUCTURE OF SILICATES





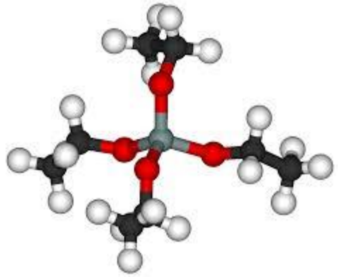
Basic structural unit

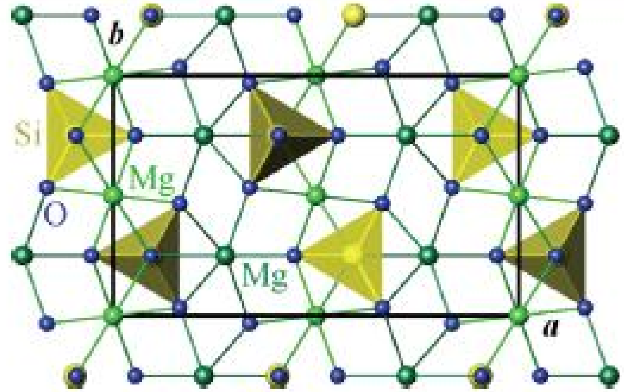
SiO_4^{4-}

- **Si** in tetrahedral coordination
- Bond type *(Pauling)*: 50% ionic -50% covalent
- $r_C/r_A = 0.29$ → stable structure with tetrahedral coordination .
- ↑ packing factor ⇒ tetrahedra united in the corners .
- Multitude of possible structures:
  - a) Structures of isolated silicates
  - b) Ring and Chain structures
  - c) Laminar structures
  - d) 3D structures

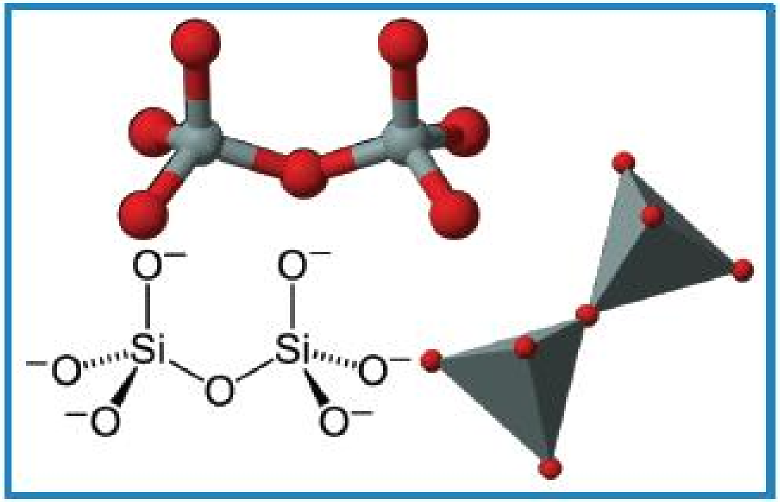
STRUCTURE OF SILICATES

Classification of silicates as a function of the tetrahedra ordering $[SiO_4]^{4-}$.

Type
•**Orthoslilicates or olivines** (island tetrahedra SiO_4^{4-}) Example: Forsterite (Mg_2SiO_4) 
•**pyroslilicate** (island tetrahedra $Si_2O_7^{6-}$) Example: ($Ca_2MgSi_2O_7$)
•**metasilicates** $(SiO_3)_n^{2n-}$ (ring and chain structures)
Ring structures Examples: Wollastonite ($CaSiO_3$), beryl $Be_3Al_2(SiO_3)_6$
chain structures Example: Enstatite ($MgSiO_3$)
•**sheet or layered silicates** $(Si_2O_5)^{2-}$ Example: Kaolinite clay $Al_2(Si_2O_5)(OH)_4$ are talc $[Mg_3(Si_2O_5)_2(OH)_2]$ micas [e.g., muscovite, $KAl_3Si_3O_{10}(OH)_2$
•**3D** (SiO_2) Quartz , tridymite, cristobalite (SiO_2)



Mg_2SiO_4 (olivine)



pyroslilicates

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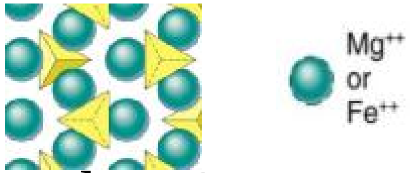
STRUCTURE OF CILICATES

The general nature of silicate structures is the connection of the SiO_4^{4-} tetrahedra. Additional oxides tend to break up the continuity of these tetrahedra. The remaining connectedness may be in the form of islands, chains or sheets:

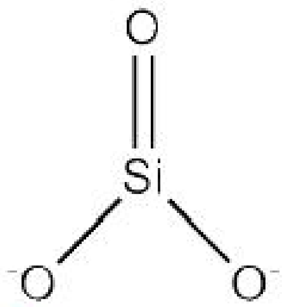
- **Network silicate structures –** these structures connect all 4 corners of the SiO_4^{4-} tetrahedra to form a *network*. The Oxygen atoms are shared which accounts for the overall chemical formula of SiO_2 not SiO_4.
- **Island silicate structures –** when positive ions bond with the oxygens of the SiO_4^{4-} tetrahedral



- **Chain or ring silicate structures –** when 2 corners of each SiO_4^{4-} tetrahedra are bonded with corners of other tetrahedra with unit chemical formula SiO_3^{-2}.
- **Sheet silicate structures –** when 3 corners in the same plane of a silicate tetrahedron are bonded to the corners of 3 other silicate tetrahedra with chemical unit $Si_2O_5^{-2}$.

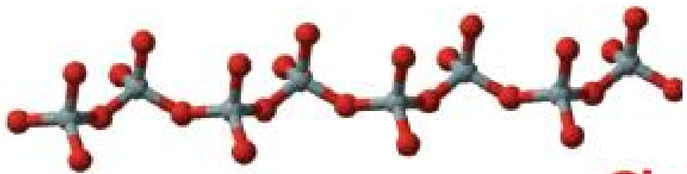
STRUCTURE OF SILICATES

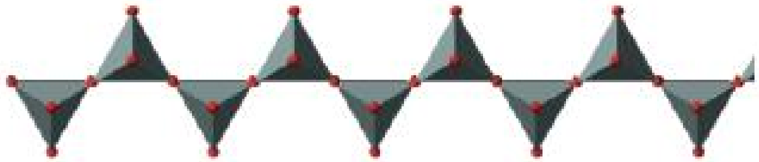
Metasilicates (Ring and Chain Structure)



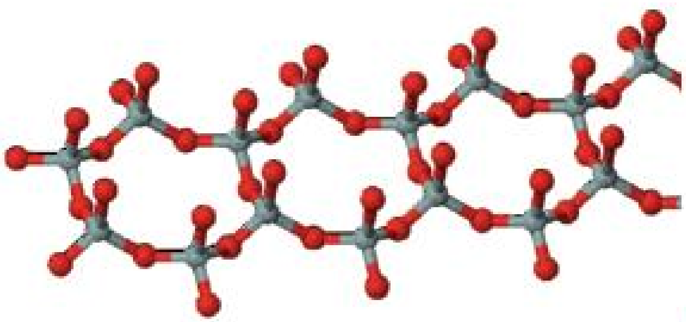
2 of the 4 O^- atoms in the tetrahedral SiO_4^{4-} are united to another tetrahedral in order to form **chains of silicate**

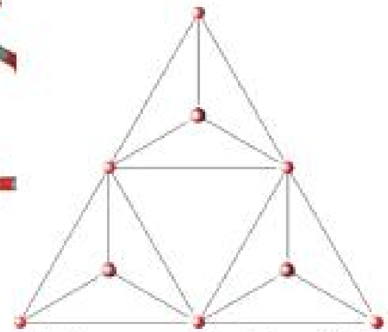
Formula: $(SiO_3)_n^{2n-}$



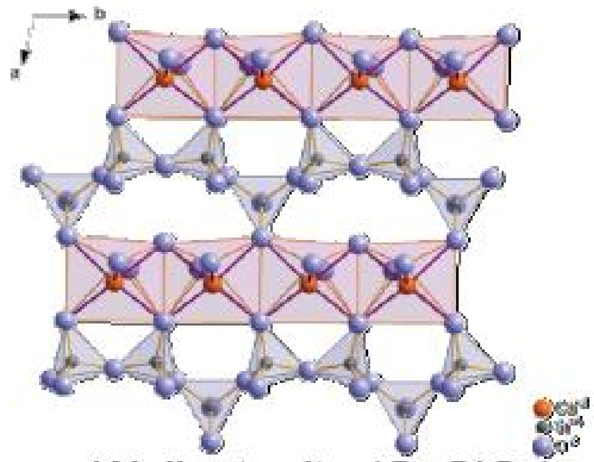


Chain Structure





http://commons.wikimedia.org/wiki/File:Cyclosilicates_3.svg



Ring Structure

Wollastonite ($CaSiO_3$)

STRUCTURE OF SILICATES

Sheet or layered structure

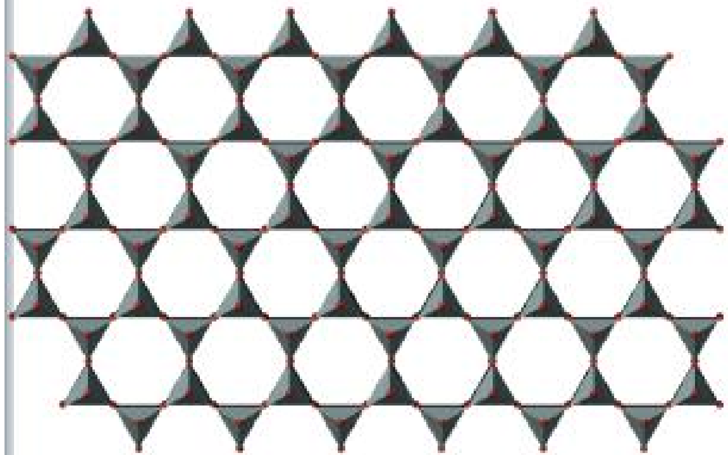
3 of the 4 O^- atoms of in the tetrahedral SiO_4^{4-} are united to another tetrahedral in order to form **layers of silicates**

Formula: $Si_2O_5^{2-}$

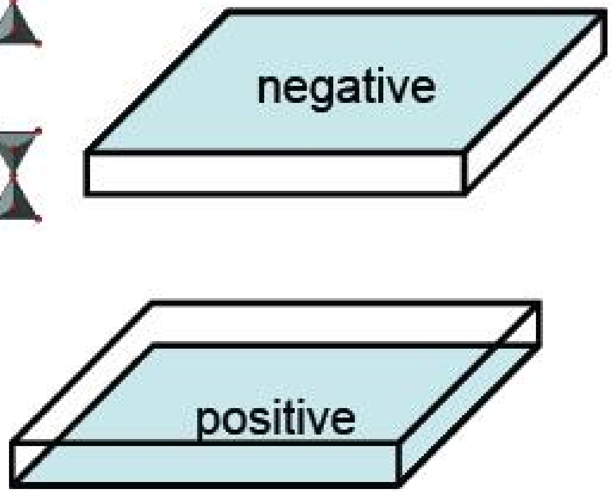
- Kaolinite $Al_2(OH)_4^{2+}$
- Talc: $Mg_3(OH)_4^{2+}$

There is one **O⁻** without bond in each tetrahedral

⇒ charge (-) ⇨ Joining laminas (+)



Formation of KAOLINITE



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STRUCTURE OF SILICATES

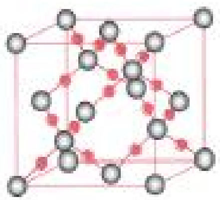
Three-Dimensional Silicates

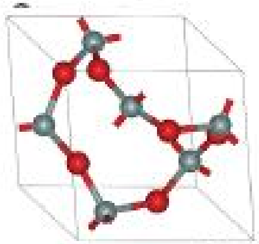
Silica

- They share all the corners in the tetrahedra
- Unit formula : SiO_2
- Presents Allotropy
- Important component in many traditional ceramics and many types of glasses

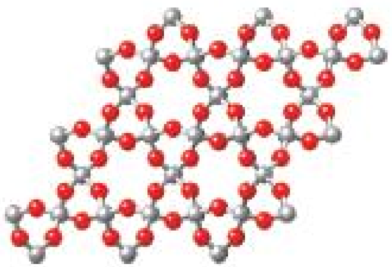
Feldspars

- Similar structure to Silica (Al^{3+} replaces Si^{4+}) ⇒ lattice with (-) charge ⇒ compensates the charge with voluminous cations (Na^+, K^+, Ca^{2+}, Ba^{2+}) in interstitial positions .
- Principal component of traditional ceramics

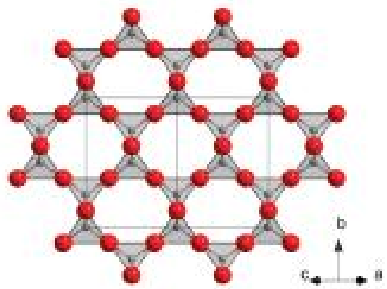




α-quartz



β-quartz



β-cristobalite