Universidad
Carlos III de Madrid
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MATERIALS SCIENCE AND ENGINEERING

TOPIC 6. CERAMIC MATERIALS

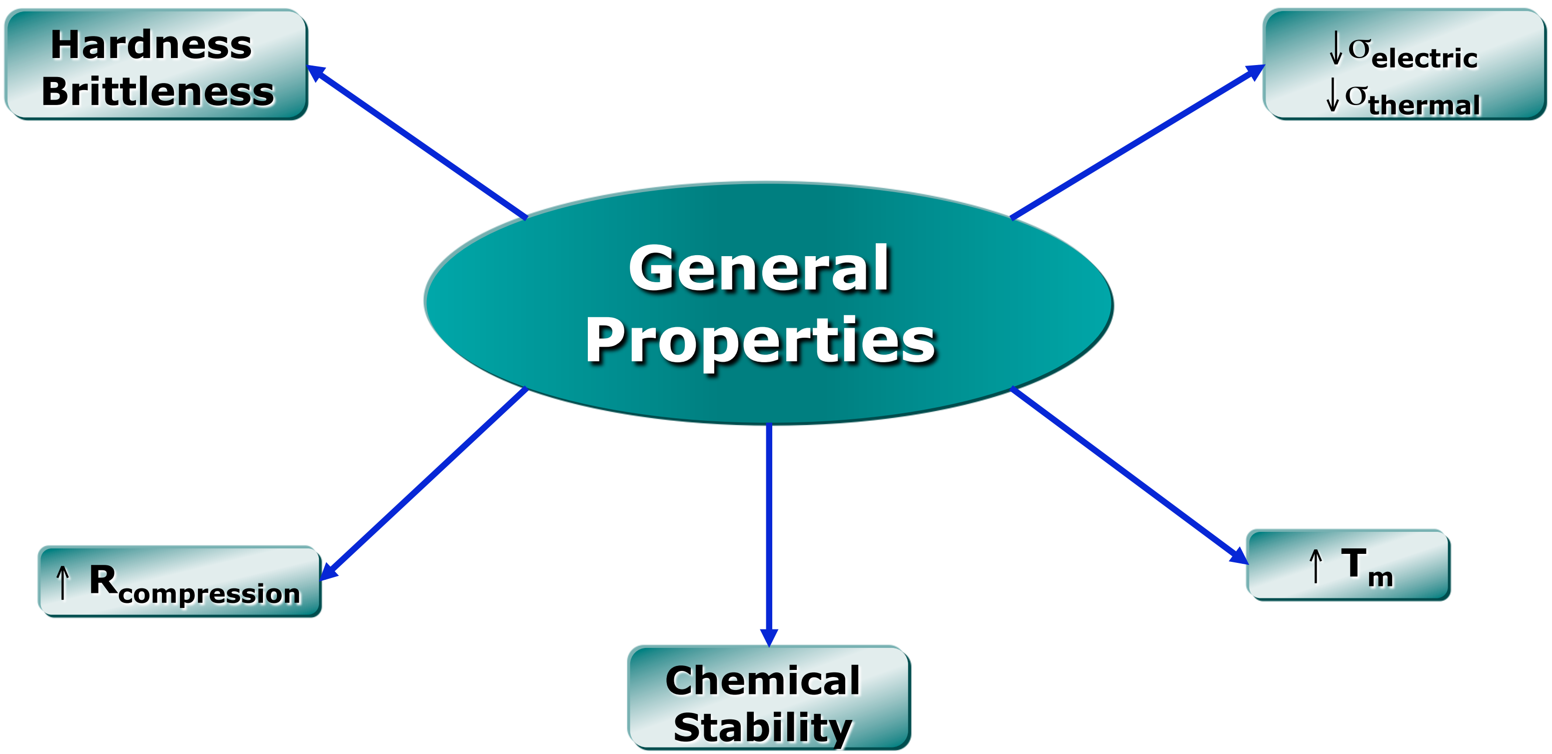
- **Introduction**
- **Structure of Ceramic Materials**
- **Glasses**
- **Mechanical Properties of Ceramic Materials**
- **Processing of Ceramic Materials**
- **Examples of applications**

INTRODUCTION

Inorganic Materials made from Metals and Non Metals united by ionic and/or covalent bonds

Can be: crystalline, amorphous or mixture of both

GENERAL PROPERTIES



GENERAL PROPERTIES

- **High Young's Modulus and high melting points**

⇒ Strong bonds (covalent and /or ionic)

- **Limited electrical and thermal conductivity**

⇒ Absence of electronic cloud (directional bond)

- **Low thermal shock resistance**

⇒ Coefficients of thermal expansion and thermal conductivity are low

- **Refractory**

⇒ Stability at high temperature (NO CREEP)

- **Resistance to oxidation/corrosion**

⇒ Chemical stability

CLASSIFICATION

Glasses

Based on SiO_2 + additives for ↓ T_f

Traditional Ceramics (clay products)

- Porous ceramics (bricks, pottery, china)
- Compact ceramics (porcelain, earthware)
- Refractory ceramics

Clay: $Al_2O_3 \cdot SiO_2 \cdot H_2O$

Silica: SiO_2

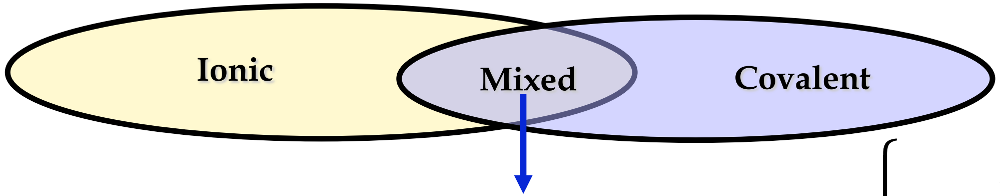
Feldspar: $K_2O \cdot Al_2O_3$ $6SiO_2$

Egineering Ceramics or Advanced Ceramics :

- Refractory ceramics (SiC, Al_2O_3, ZrO_2, BeO, MgO).
- Piezoelectrics and Ferroelectrics: $BaTiO_3$, $SrTiO_3$
- Electro-optics: $LiNbO_3$
- Abrasive ceramics: nitrides and carbides Si_3N_4 , SiC
- Molecular membranes
- Superconductive ceramics ($YBa_2Cu_3O_7$)
- Biomaterials : Hydroxyapatite

STRUCTURE

Ceramic Bonds



Pauling: % 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
SiC	Si-C	0,7	11	89

STRUCTURE

T2 STRUCTURES:

- Ions packing
- Electroneutrality of ionic ceramics
- Crystalline type structures

ELECTRONEUTRALITY IN IONIC CERAMICS

Ionic structure : packing of anions with cations in interstitials

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

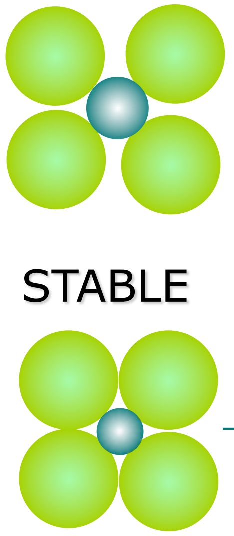
Sizes C^+ A^- ⇨ ($r_{cation} < r_{anion}$)

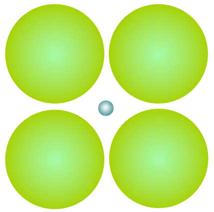
Electroneutrality

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

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

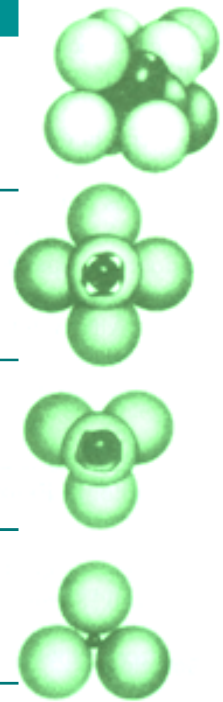
PACKING OF IONS



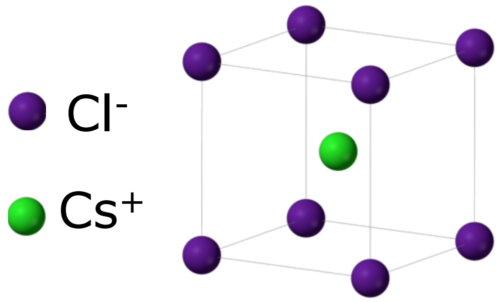


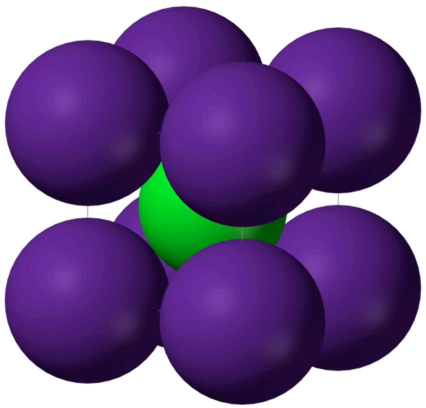
The relation between radius when A^- and C^+ are in contact ⇨ **Relation of radius is critical** (*minimum*)

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



SIMPLE CUBIC STRUCTURE: CsCl



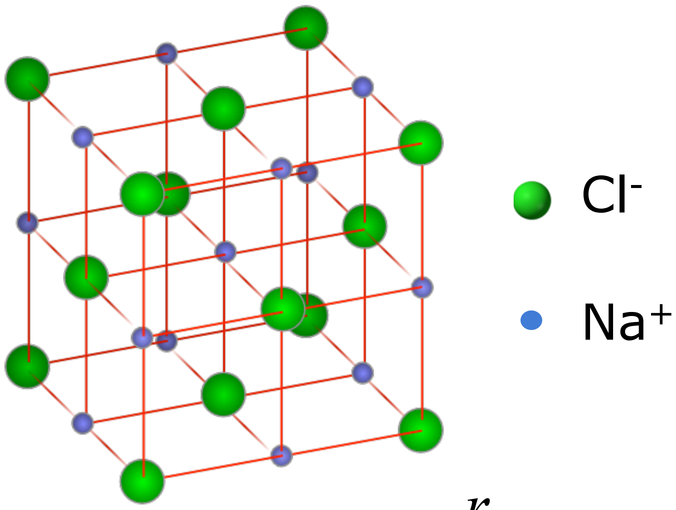


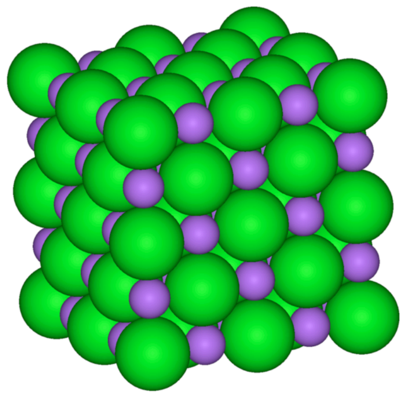
- Cl^- : cubic
- Cs^+: centre of the cube
- C.I.: 8

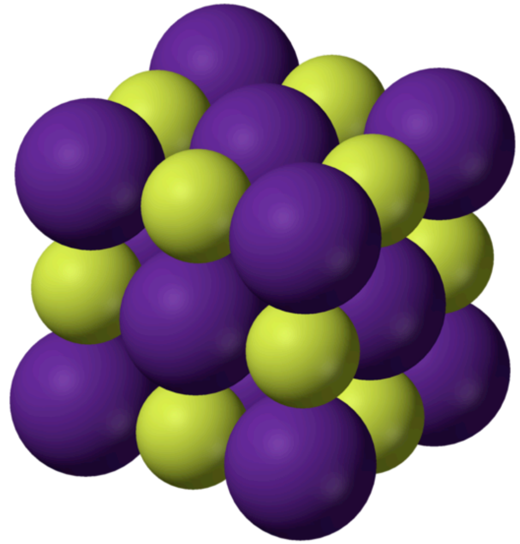
$$\frac{r_{Cs^+}}{r_{Cl^-}} = 0{,}94 > 0{,}732 \Rightarrow C.I. = 8 \Rightarrow \text{Cubic structure}$$

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

FCC STRUCTURE: NaCl





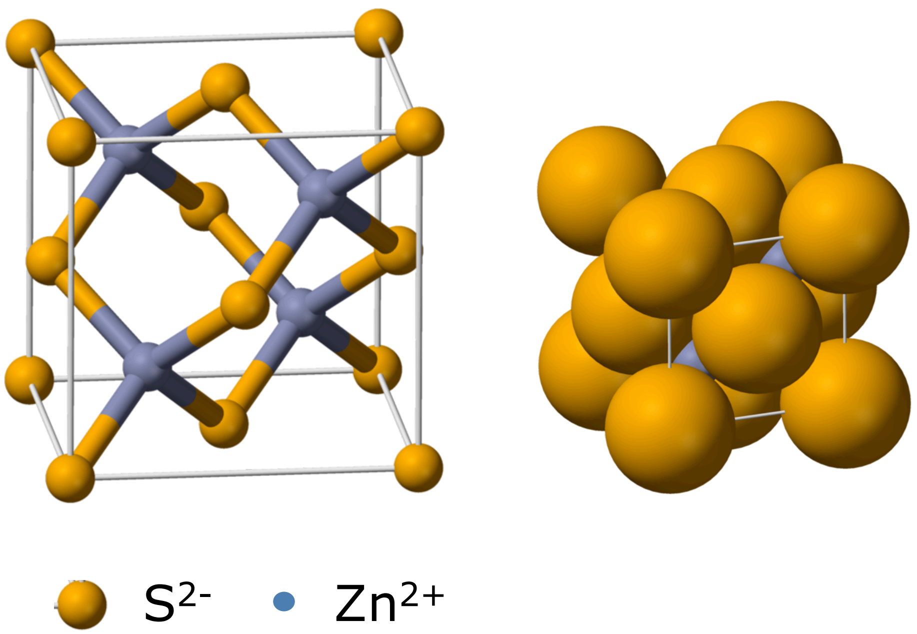


$$\frac{r_{Na^+}}{r_{Cl^-}} = 0,56 > 0,414 \Rightarrow C.I. = 6 \Rightarrow \text{Octahedral coord.}$$

- 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

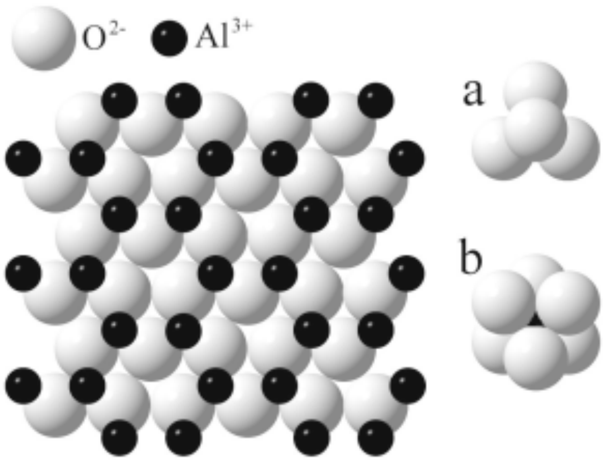
$$\frac{r_{Zn^{2+}}}{r_{S^{2-}}} = 0.345 \Rightarrow C.I. = 4$$

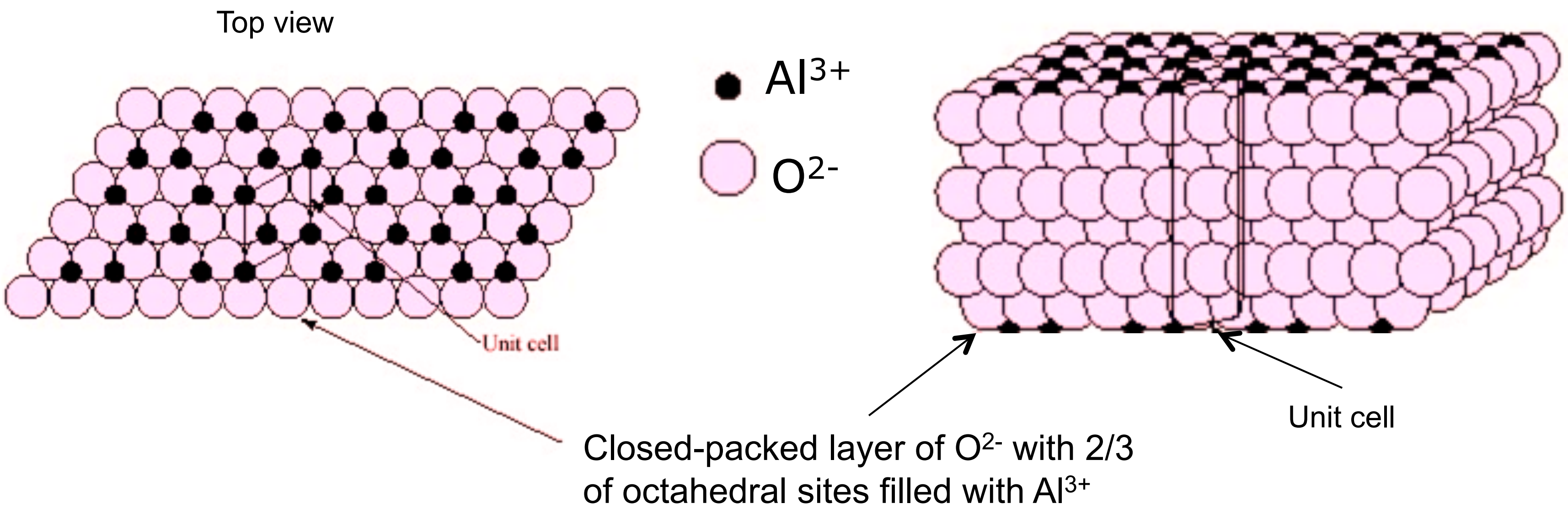
According to Pauling bond **Zn-S ~87% covalent**

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

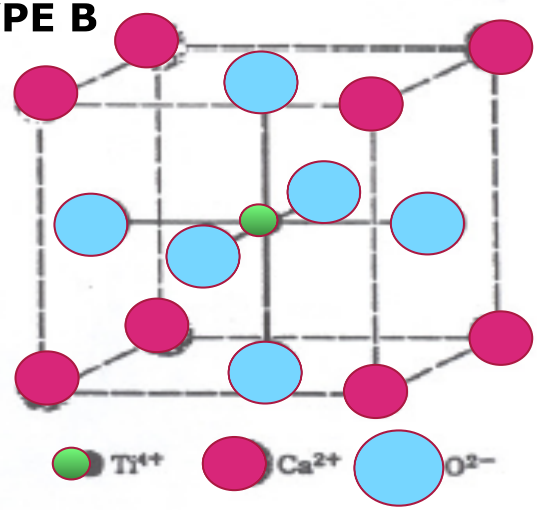


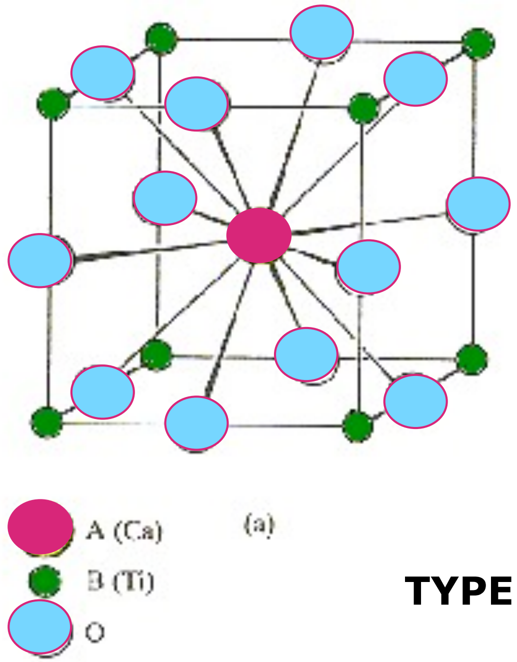


Ceramics that have this type of structure: **Cr_2O_3, Fe_2O_3, Al_2O_3 …**

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	$MgAl_2O_4$, $FeAl_2O_4$

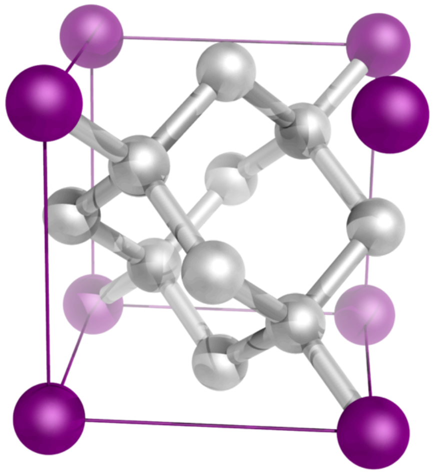
COVALENT CERAMICS

They are structural ceramics

DIAMOND → Structure type blend

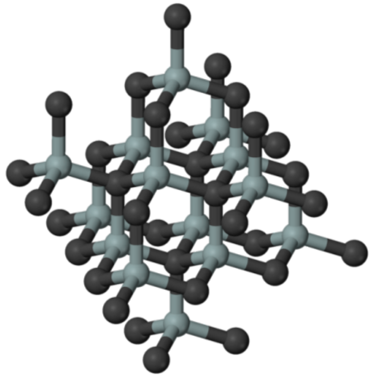
C→ sp³ → c.i. 4 → Tetrahedral CC_4. Bond 100% covalent.

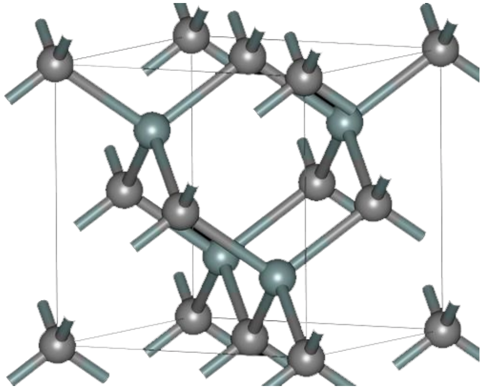
- ↑ wear resistance ↑ hardness
- ↑ tensile strength Insulator



SiC → Diamond type structure (spherullite)

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





COVALENT CERAMICS

They are structural ceramics

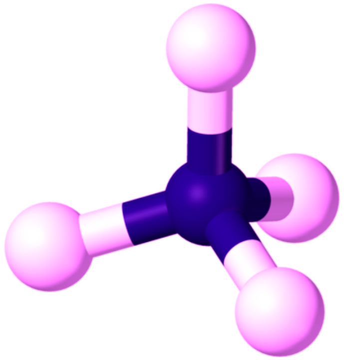
Si_3N_4 → Cutting Elements, blades, rotors

Si → sp^3 → c.i. 4 → SiN_4 Tetrahedra

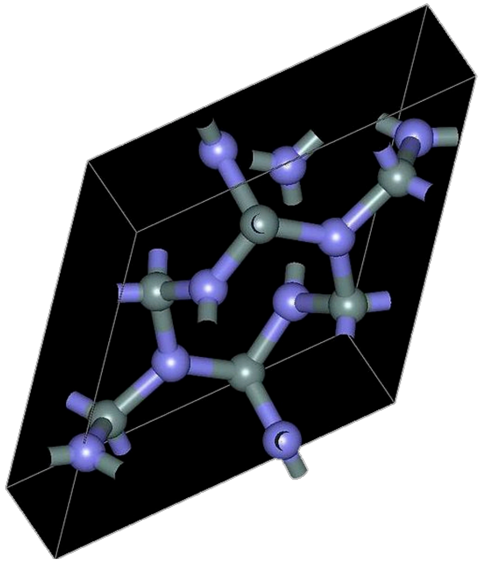
N → sp^2 → c.i. 3 → N coordinated to 3 Si

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

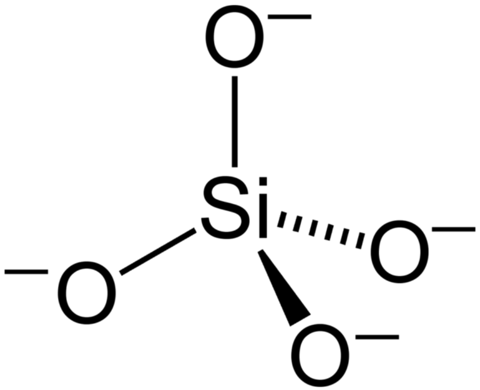
	Composition (wt%)					
Ceramic	SiO_2	Al_2O_3	K_2O	MgO	CaO	Other
Silica refractory	96					4
Fireclay refractory	50-70	45-25				5
Mullite refractory	28	72				-
Electrical porcelain	61	32	6			1
Steatite porcelain	64	5		30		1
Portland cement	25	9			64	2

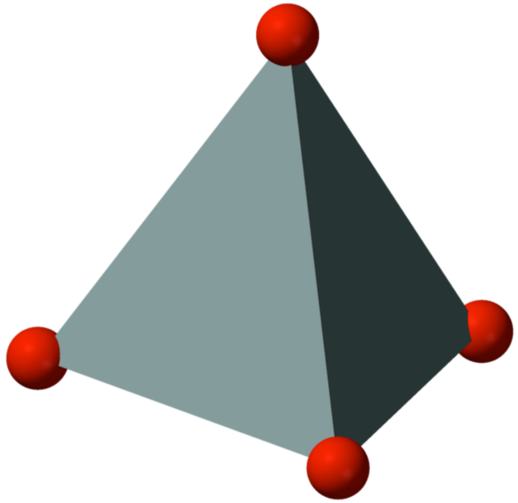
Composition of some silicate ceramics

Fundamentally in:

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

STRUCTURE OF SILICATES





Basic structural unit

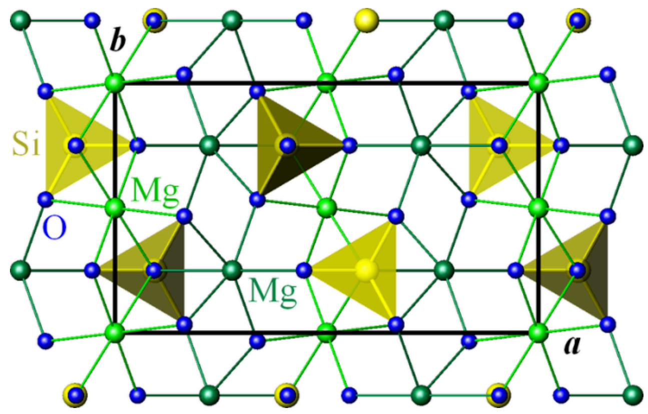
SiO_4^{4-}

- **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

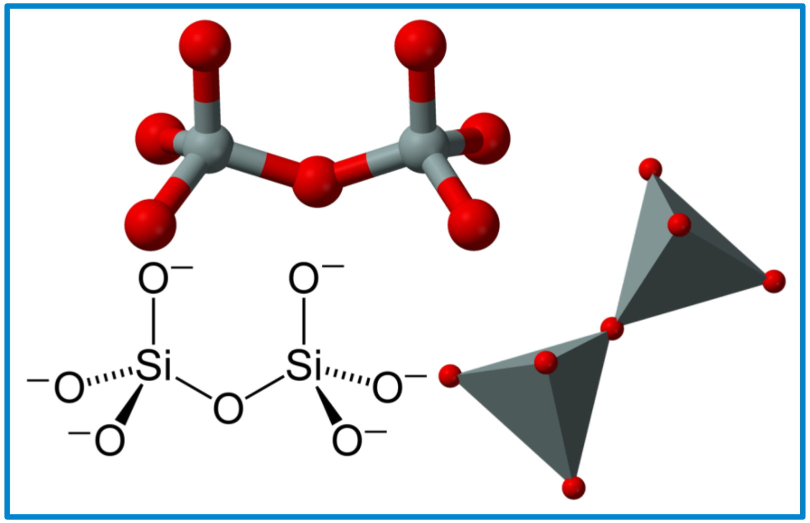
STRUCTURE OF SILICATES

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)



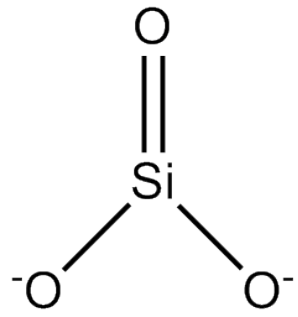
Mg_2SiO_4 (olivine)



pyroslilicates

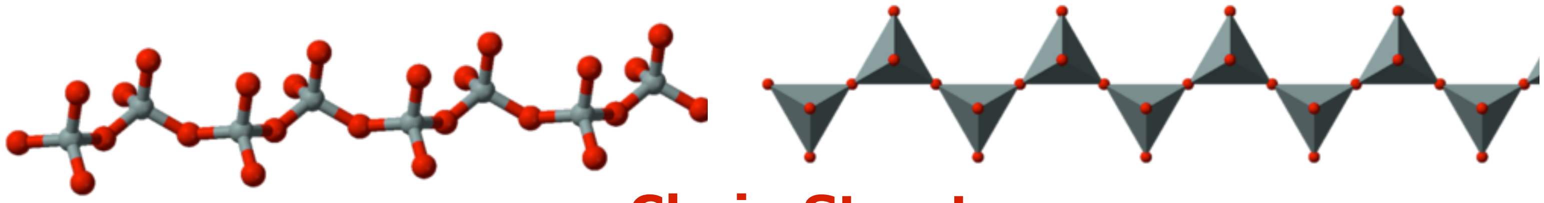
STRUCTURE OF SILICATES

Metasilicates (Ring and Chain Structure)

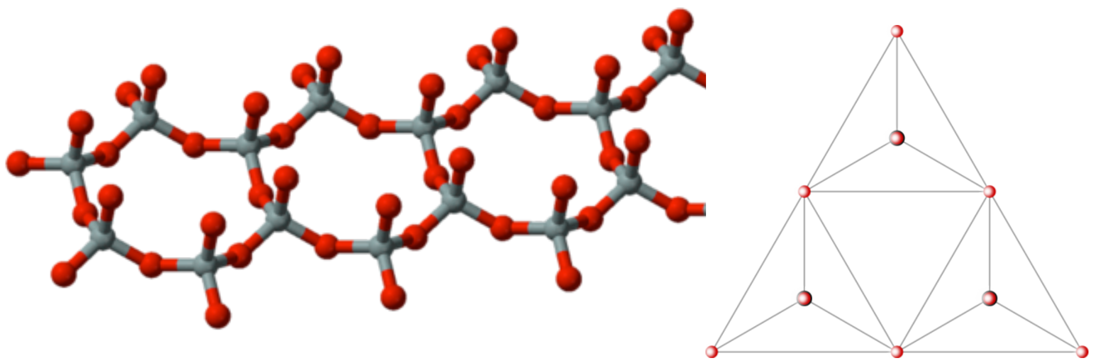


2 of the 4 O^- atoms in the tetrahedral SiO_4^{4-} are united to another tetrahedral in order to form **chains of silicate**

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

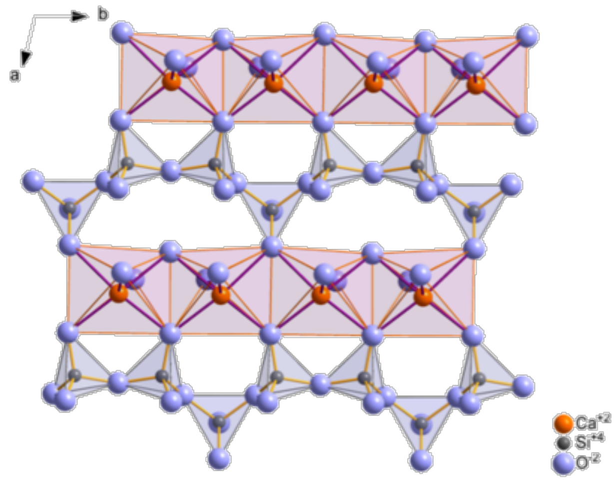


Chain Structure



Ring Structure

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



Wollastonite ($CaSiO_3$)

http://commons.wikimedia.org/wiki/File:Wollastonite_a_%2B_c.png

STRUCTURE OF SILICATES

Sheet or layered structure

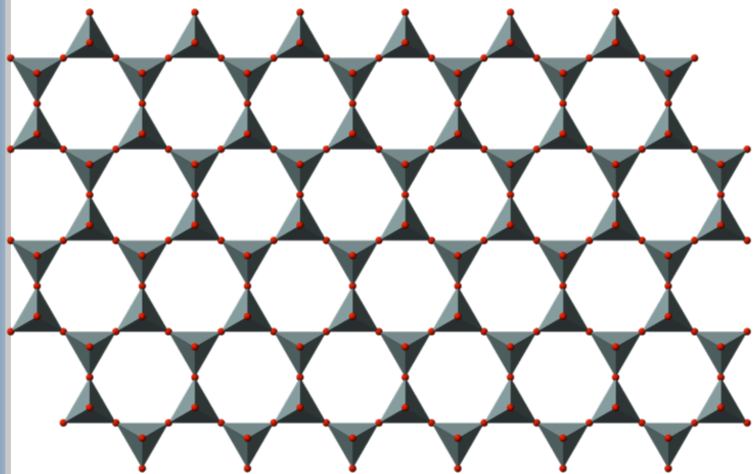
3 of the 4 O^- atoms of in the tetrahedral SiO_4^{4-} are united to another tetrahedral in order to form **layers of silicates**

Formula: $Si_2O_5^{2-}$

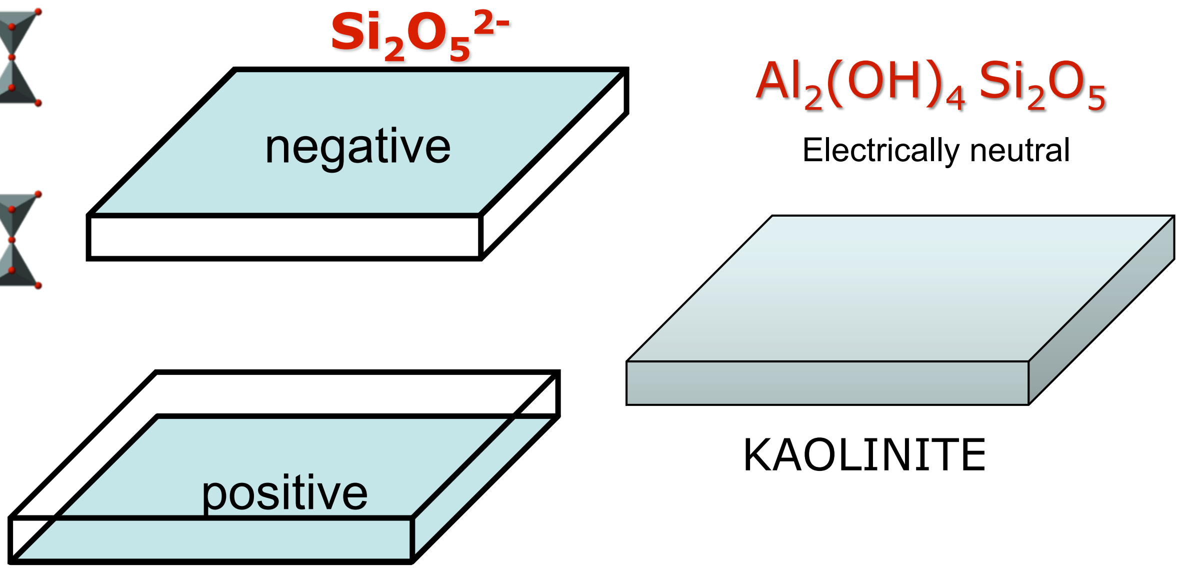
- Kaolinite $Al_2(OH)_4^{2+}$
- Talc: $Mg_3(OH)_4^{2+}$

There is one **O^-** without bond in each tetrahedral

⇒ charge (-) ⇨ Joining laminas (+)



Formation of KAOLINITE



STRUCTURE OF SILICATES

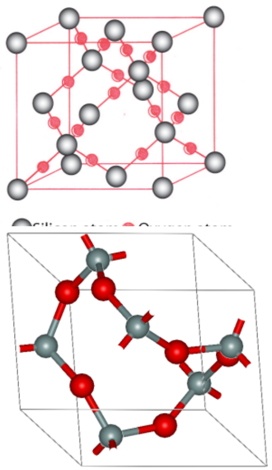
Three-Dimensional Silicates

Silica

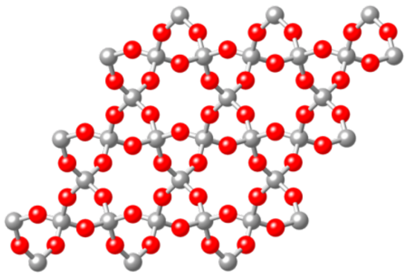
- They share all the corners in the tetrahedra
- Unit formula : SiO_2
- Presents Allotropy
- Important component in many traditional ceramics and many types of glasses

Feldspars

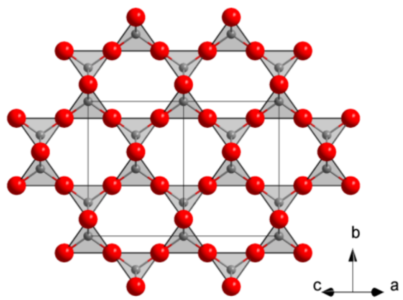
- Similar structure to Silica (Al^{3+} replaces Si^{4+}) ⇒ lattice with (-) charge ⇒ compensates the charge with voluminous cations (Na^{+}, K^{+}, Ca^{2+}, Ba^{2+}) in interstitial positions .
- Principal component of traditional ceramics



α-quartz



β-quartz



β-cristobalite

NON CRYSTALLINE CERAMICS : GLASSES

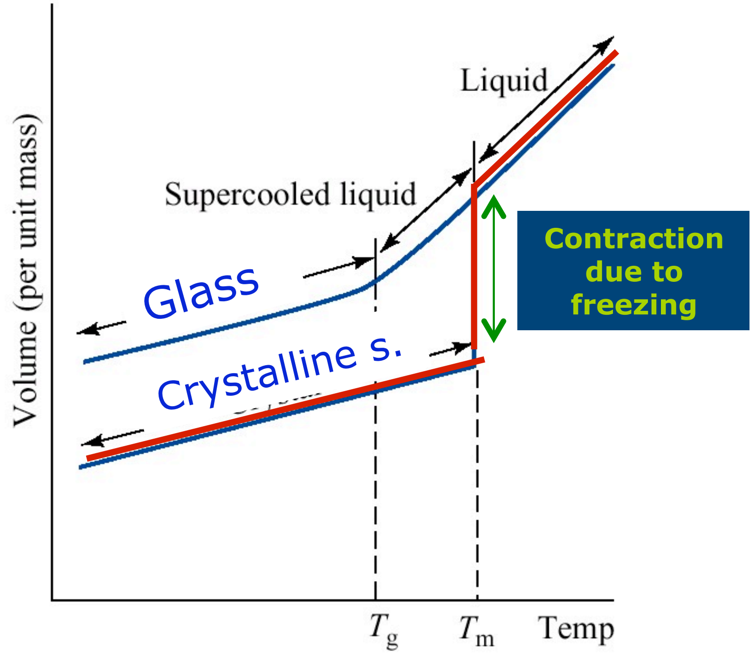
Behaviour of glass during solidification

Crystalline Solid

As ↓T crystallizes in T_m

GLASS

As ↓T: ↑viscosity
Plastic stage ⇔ Rigid stage



CONSTITUENTS OF GLASSES

3 types of oxides

Glass Formers

SiO_2 and B_2O_3

- **SiO_2: Fundamental** sub-unit : **SiO_4^{4-} tetrahedra**
- **B_2O_3: Fundamental** Sub-unit : plane triangles BO_3^{3-} ⇨ triangles BO_3^{3-} become BO_4^{4-} tetrahedra when we add oxides of alkaline M and alkaline earths. The cations give electroneutrality. The glasses that are made only of B_2O_3 have little durability .
- Normally we add B_2O_3 to SiO_2: ***borosilicate glasses***

Glass modifiers

(Na_2O, K_2O) and (CaO and MgO)

- Are the oxides that **brake the silicate lattice**
- Alkaline (Na_2O, K_2O) alkaline earths (CaO y MgO)
- They are accommodated in interstitials (do not form part of the silicate lattice)
- ↓ **viscosity** ⇨ facilitates moulding and workability

Intermediates: Al_2O_3

DO NOT form glasses only by themselves.

They are incorporated in the silicate lattice

- **Al_2O_3** ⇨tetrahedra AlO_4^{4-} replacing SiO_4^{4-}
- **Charge defects** (Al^{3+}: Si^{4+}) compensating with alkaline cations and alkaline earths .

Improve special properties :

- **Al_2O_3** ⇨ ↑ strength at high T (***aluminosilicate glasses)***
- **PbO**
  - Modifies optical properties
  - ↓ T_f (glass soldering)
  - Radiation protection of ↑ E

CONSTITUENTS OF GLASSES

Substances constituents of glasses

COLOURS THAT METALLIC IONS GIVE TO GLASSES		
	M^+ as a MODIFIER	
ION	C. I.	COLOUR
Cr^{3+}	6	Blue
Cr^{6+}	6	Green
Cu^{2+}	8	Blue –green
Cu^{+}	6-8	Transparent
Co^{2+}	6-8	Rose
Ni^{2+}	8	Yellow –green
Mn^{2+}	6	Light orange
Mn^{3+}	6-8	
Fe^{2+}	6	Blue-green
Fe^{3+}	6-10	Light yellow
U^{6+}	6	Light yellow
V^{3+}	6	Green
V^{4+}		Blue

PROPERTIES OF GLASSES

Mechanical Properties

Brittle Materials (↑↑ elastic modulus) = f (composition, macroscopic (surface) imperfections, volume of material and T)
Low modulus of Weibull
Mechanical strength ↓ (presence of water/air + humidity)

Electrical Properties

Generally insulators ($\sigma \approx 10^{-10}$ - 10^{-20} Ωcm^{-1})
σ↑↑ with Temperature
σ↑↑ with modifier (=f(size and amount of modifier))

Thermal Shock

$\uparrow\uparrow\alpha = \downarrow R_{thermal\ shock}$

Material	Thermal Expansion coeff. ($^{o}C^{-1}$)	Thermal Shock failure (^{o}C)
Soda-lime glass	10^{-5}	80
Sodium borosilicate (Pyrex ™ type)	10^{-4}	270
Fused silica	10^{-6}	1600
Lithia-alumina-silicate glass ceramic (Pyroceram ™ type)	10^{-6}	670
Transparent lithia-alumina-silicate glass ceramic (Visions ™ type)	10^{-6}	1330

Thermal shock resistance of common glasses and glass ceramics