

MM-101

Theory

Chapter no. 12 :-

Structures & properties of Ceramics.

Q. Define Ceramics:-

Ceramics are non-metal, inorganic materials that are typically made from clay and other natural raw materials through the process of heating and cooling.

They are known for their;

- (i) hardness
- (ii) Brittleness
- (iii) High melting points.
- (iv) Resistance to heat and Chemical attacks.

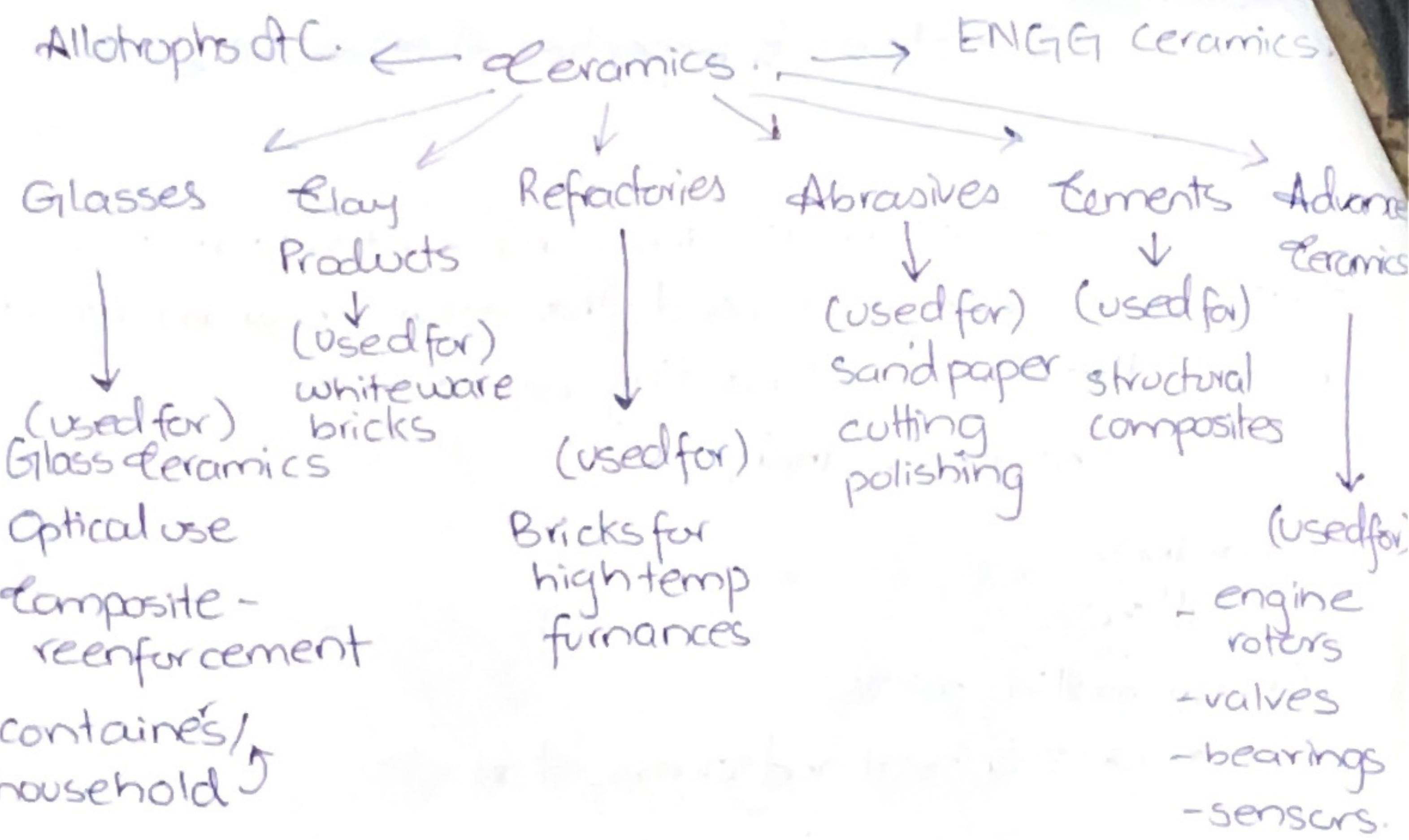
Q. Describe the structure of Ceramic materials.

How do they differ from that of the metals?

The structure of the ceramics differ from that of the metals, based on their atomic bonding and crystal structure, eventually affecting their properties.

- (i) Ceramic such as $\overset{\text{metal}}{\text{Al}_2\text{O}_3}$ $\overset{\text{nonmetal}}{\text{SiC}}$ are composed of ionic bonds, and ceramics such as SiC are composed of covalent, while metals contain metallic bonding which contains a sea of electrons that move freely along a lattice structure.
- (ii) Ceramics have complex crystal structures as compared to metals that have simple FCC, BCC, HCP crystal structures.
- (iii) Ceramics ionic/covalent bonds are directional in nature (\therefore brittle)
Metals metallic bonds are non-directional in nature (\therefore ductile)

Taxonomy of Ceramics:-



- * Glass Ceramic is a fine grained poly crystalline material.
- * Engineering Ceramics include:

- Oxides
- Nitrides
- Carbides
- Optical fibers.

Q. How does atomic bonding in Ceramics is determined between Ionic or Covalent.

Atomic bonding ranges from purely ionic to totally covalent. Mostly ceramics are ionic in nature but some are also covalent.

$\Rightarrow (\Delta)$ % ionic character increases with Δ in difference in electronegativity.

$\therefore \text{CaF}_2 \rightarrow 89\% \text{ IC}$ while SiC with $12\% \text{ IC}$ is covalent.

Describe the crystal structure of ionic ceramics.

The crystal structure of a ionic ceramic by three underlying concepts:

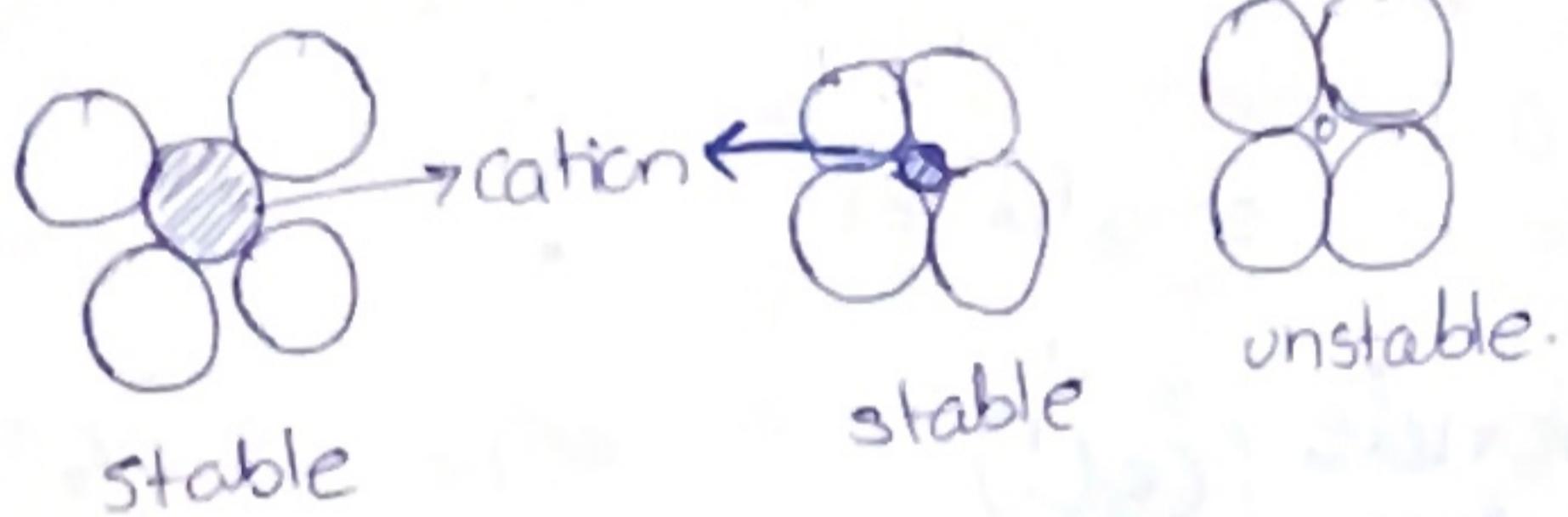
- (i) charge Neutrality
- (ii) Ionic Radii of Cations(r_c) & Anions(r_a)
- (iii) Neighbouring particles/stability

The ceramic's cations are balanced by anion for a always neutral overall charg.



As metals tend to lose electrons
 $\therefore r_c < r_a$ and r_c/r_a is < 1 .

The ceramic's crystal structure's stability occurs when anions surrounding cations) are in contact with the cation.



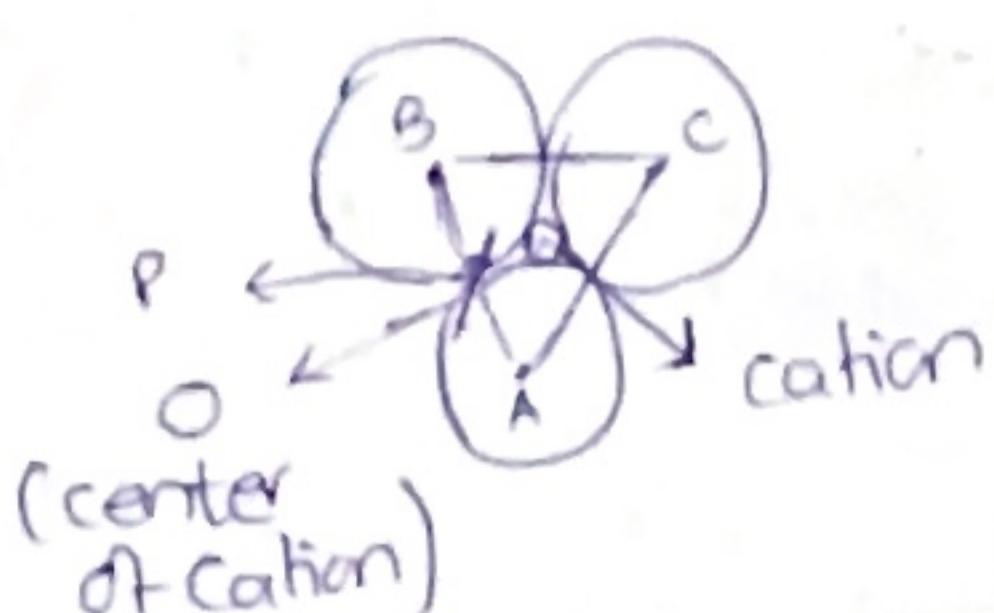
Q. Difference between metals and ceramics (slide 4)

NUMERICAL:

Show that the minimum cation-to-anion ratio for the coordination no.3 is 0.155.

As coordination no.3 \Rightarrow the number of ions that are attached with the central atom (i.e cation).

Combining all 3 centres of anion forms an equilateral Δ ; $\alpha = \beta = \gamma = 60^\circ$



$$\text{Now } \frac{\cos \alpha}{\sin \alpha} \Rightarrow \frac{r_A}{r_A + r_C}$$

$$\frac{r_A}{r_A + r_C} > 0.1555 \text{ Ans!}$$

Let \overline{AP} be the radius of anion

$$AO \Rightarrow r_A + r_C$$

Now join to form $\Delta P O A$

$\angle \alpha$ where $\alpha = 30^\circ$ due to half of 60° from ΔABC

Q. Describe the AX-Type Crystal Structure Ceramics with examples.

examples.
Some ceramics have "equal no. of cations and anions"
this is referred as AX-Type where ($A \Rightarrow$ Cation, $X \Rightarrow$ Anion)
Following are its examples:- (specific Structure)

(i) Rock Salt (NaCl / MgO etc)
Structure.

$$\text{(Not needed)} \quad r_C/r_A \Rightarrow \approx 0.414 - 0.732 \\ \text{(Needed)} \quad \text{exactly} \Rightarrow 0.563.$$

$$r_C = 0.102 \text{ nm}$$

$$r_A = 0.18 \text{ nm}$$

* generated from the FCC structure of cations and anions.

cations and anions.

(iii) Cesium chloride ($\text{Cs}^+ \text{Cl}^-$)
Crystal structure

$$C.N_{\text{anions}} = C.N_{\text{cation}} = 8$$

Cube \rightarrow centre $\frac{1}{8} \text{Cs}^+$
 \rightarrow corner $8 \times \frac{1}{8} = 1 \text{Cl}^-$

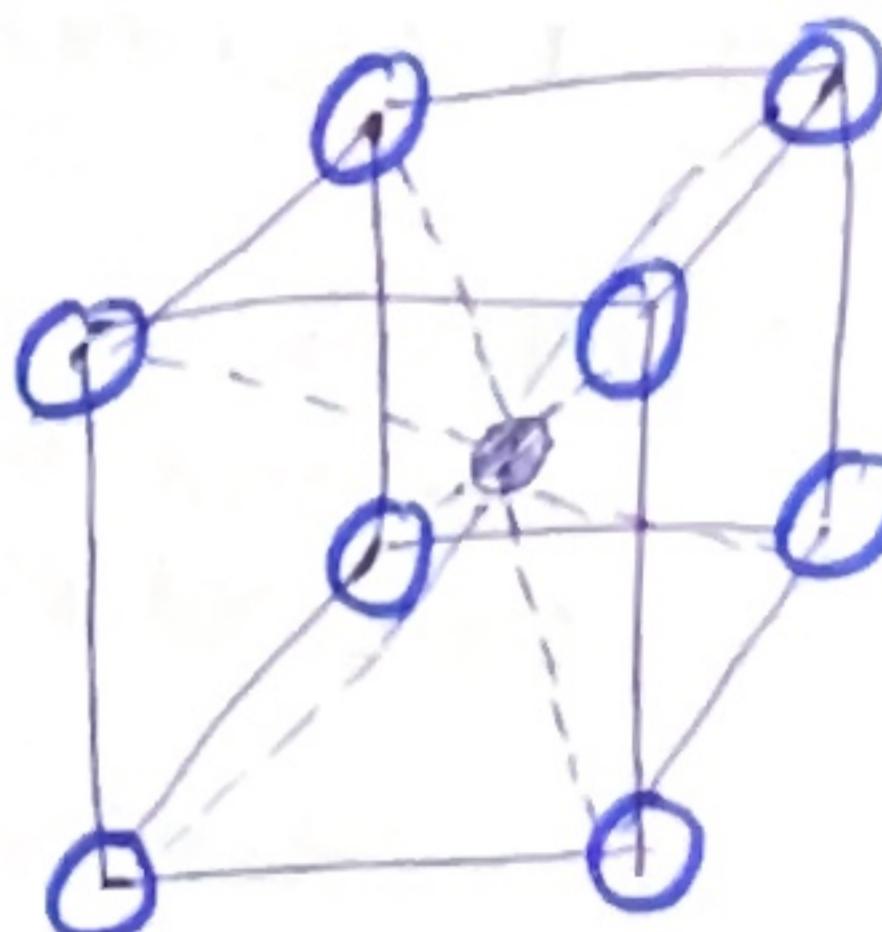
Case 7: \rightarrow corner $8/8 = 1$ (c.f.)
Not a BCC structure as 2 different types of atoms involved by relative positions of anions & cations (interchange of Anion & Cation)
structure. (position is 12-2 possible)

(iii) Zinc Blende (ZnS)
Crystal Structure.

ZnS has 18% ionic and 82% covalent character

$$\text{CN}_{\text{anions}} = \text{CN}_{\text{cations}} = 4$$

$$\text{Cube Corners} \Rightarrow \text{Silicon} \Rightarrow 8/8 = 1$$
$$\text{Cube faces} \Rightarrow " = 6/2 = 3$$

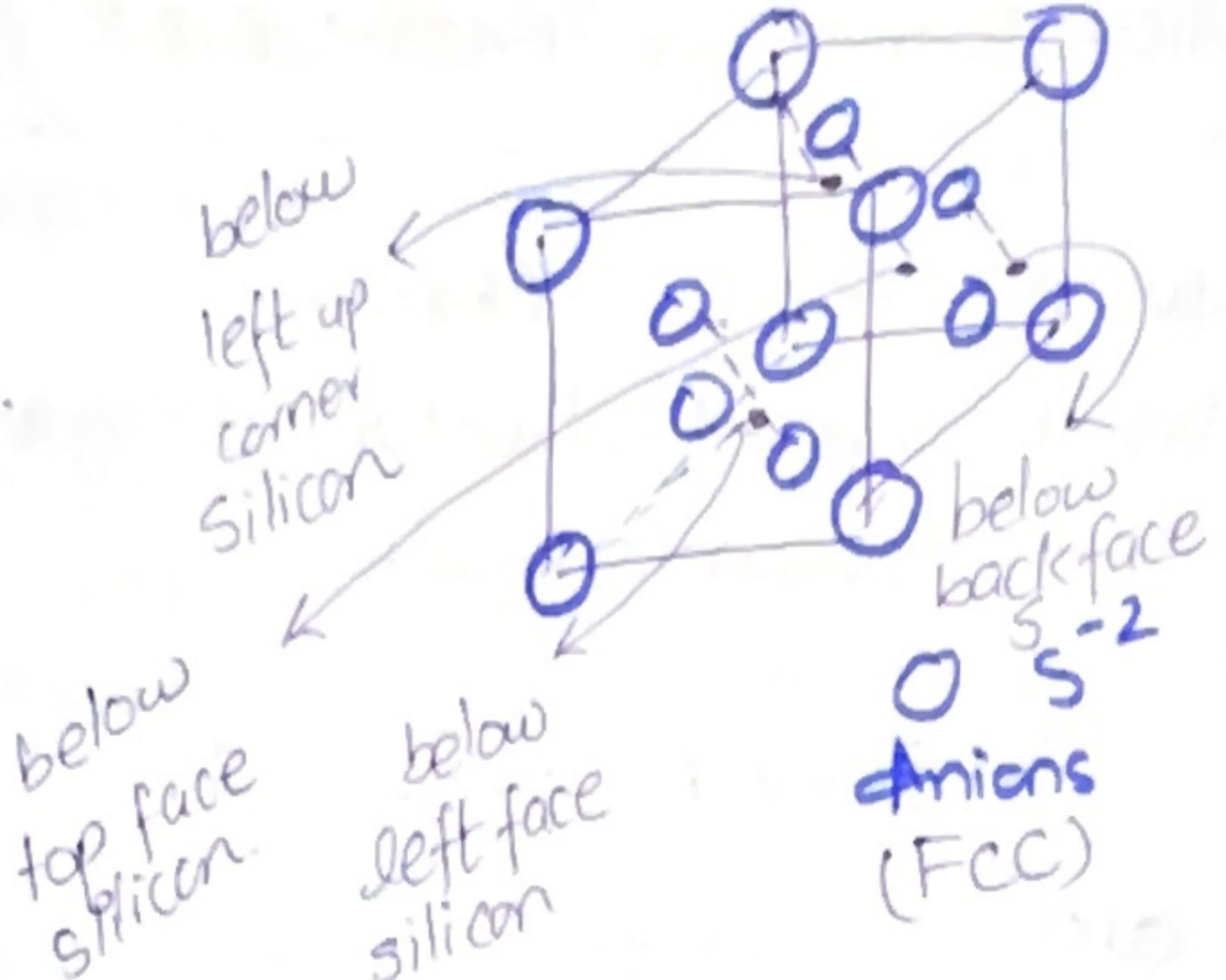


$$\text{Cs}^+ \quad \text{Cl}^-$$

$$\begin{aligned} \text{cube corners} &\Rightarrow \text{Silicon} = 8/8 = 1 \\ \text{cube faces} &= 7 \quad " = 6/2 = 3 \end{aligned}$$

Zn^{+2}

Tetrahedron Centre = 2.



- * in ZnS structure all anions/cations are tetrahedrally coordinated

* an equivalent structure will be obtained if Zn & S positions are reversed.

- * Each Zn atom is bond to 4 S atoms and vice versa.
- * usually covalent compound exhibit this structure.

a) Q. Describe the AmX_p -Type Crystal Structure for ceramics.

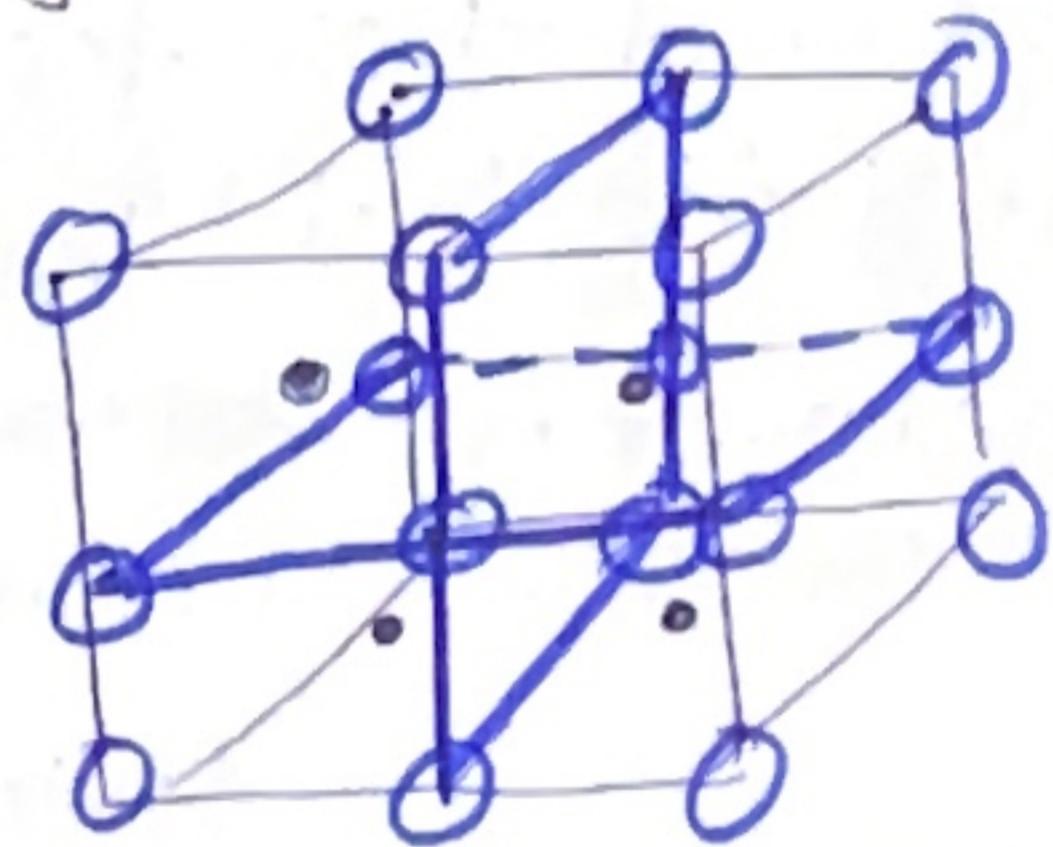
In this type the charges on cation & anions are not the same. Example CaF_2 .

$$r_{\text{Ca}}/r_{\text{F}} \approx 0.8$$

c. No \Rightarrow 8 cation, CN \Rightarrow 4 anion

structure $\Rightarrow \text{CsCl}$

One unit cell \Rightarrow 8 cubes.



Ca \bullet at the centre of 4 cubes
F O at all corners of " "

Q. Describe the AmBnX_p Type Crystal Structure for ceramics.

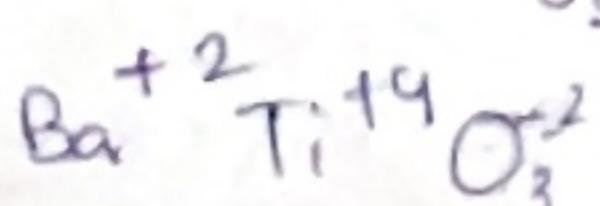
CN \Rightarrow 12(A) cation

$\Rightarrow (8-2) \Rightarrow 6(B)$

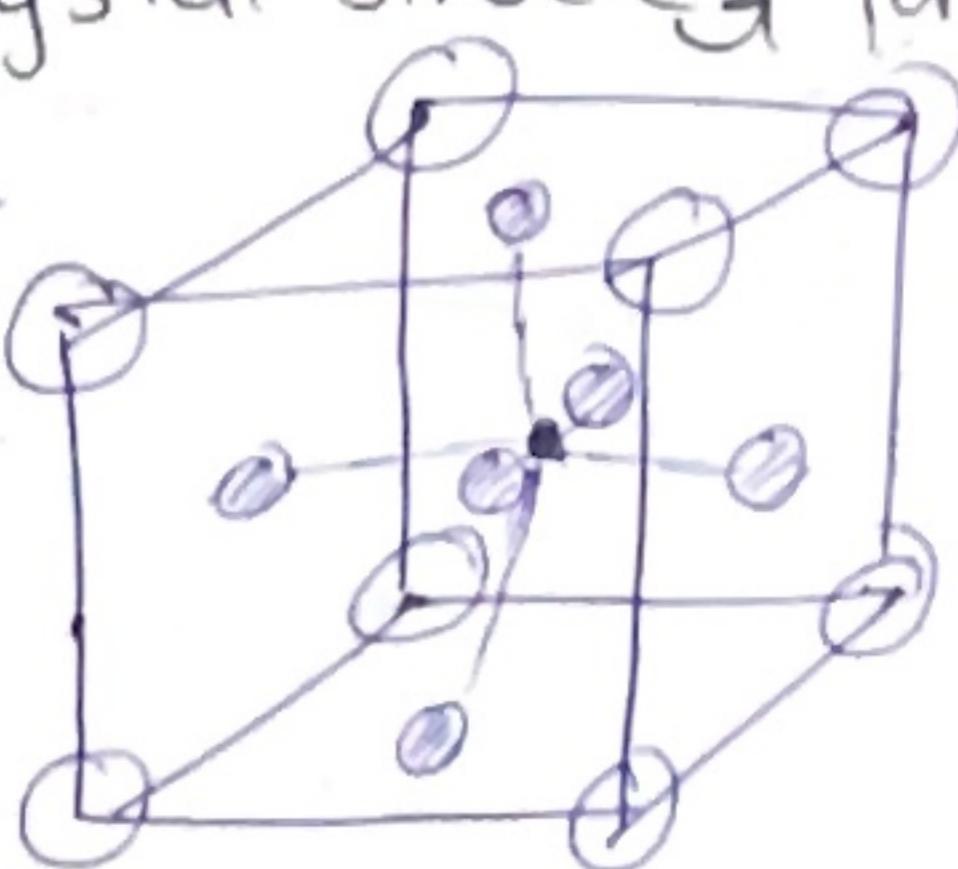
CN \Rightarrow 4 anion

- ii) The type AmBnX_p describes for the ceramics that contain more than one cation.

iii) E.g. "Perovskite Crystal Structure" in BaTiO_3



Baum Titante.



O \rightarrow Ba+2 \rightarrow corners

• \rightarrow Ti+4 \rightarrow Centre

O2- \rightarrow O \rightarrow Face

SLIDE 8 IMP. → MEMORIZE IT.

NUMERICAL 12.2 (EXM):-

What crystal structure do you predict of FeO on the basis of atomic Radii.

FeO \Rightarrow A_xX compound. \therefore CN = 6.

also

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{r_{\text{Fe}}}{r_{\text{O}_2}} = \frac{0.077}{0.140} \Rightarrow 0.550.$$

\therefore lies between

0.414 \rightarrow 0.732
and hence has a
NaCl/rock salt
structure.

Q. On what factors does the size of an ion depend?

Ion size depends on several factors but one of these factors is the (i) coordination Number. It is stated that "Ionic radius of ions increase as the no. of nearest neighbour(s) ions of opposite charge increases." Example:-

Ionic Radii of CN = 8 $>$ Ionic Radii of CN = 6 $>$

Ionic Radii of CN = 4.

(ii) charge on the ion:-

The charge on the ion also influences its radii

$\text{Fe}^{+3} \Rightarrow 0.069 \text{ nm}$

$\text{Fe}^{+2} \Rightarrow 0.077 \text{ nm}$

$\text{Fe atom} \Rightarrow 0.124 \text{ nm.}$

* Conversely the size increases with addition of valence e⁻.

When an atom is removed from it, the remaining valence e⁻s are more tightly bounded to the nucleus and thus the size decreases.

Slide : 22 + 23 imp!
UNDER SUBHEADINGS, describe the imperfections in ceramics.

a. ATOMIC DEFECTS:-

primary atoms that makeup the bulk of the ceramic materials.

Atomic defects in the host atoms may exist in ceramics. These defects can vary from being vacancies to interstitials.

Vacancies:-

(i) Cation Vacancy: A missing positive ion in the crystal lattice ($\text{Al}_2\text{O}_3 \rightarrow \text{Al}_2^{+3}$ missing)

(ii) Anion Vacancy: A missing negative ion in the crystal lattice. ($\text{Al}_2\text{O}_3 \rightarrow \text{O}_3^{-2}$ missing).

INTERSTITIALS:-

(i) Cation Interstitial: An extra cation[↑] in the normally empty spaces / interstices of a lattice.

(ii) Anion Interstitial: An extra anion positioned in the normally empty space / interstices of a lattice.

Frankel defect:-

A cation is displaced from its normal lattice site to an interstitial site, creating a vacancy-interstitial pair. (Ratio of Cation & anion is not altered).

Substitution Defect:- Occurs when an atom's ions

are replaced by another atom's ions e.g. $\text{ZrO}_2 \rightarrow \text{ZrO}_1^{+4}$ replaced with

(Ratio of Cations & Anions altered)
(is not Schottky Defect:-)

Y^{+3} ions.

A defect in which equal no. of (or taken out/placed outside) cations and anions are missing from the lattice such that; the charge neutrality is maintained.

Equilibrium conc of defects is $\sim e^{-\Phi P_A}$

Q. Define the following terms.

(i) Electric Neutrality.

state of equal no. of +ve & -ve ions.

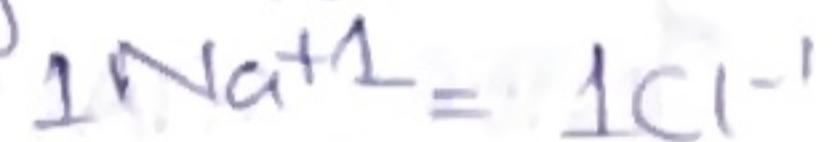
(ii) Defect structure:-

↳ often used to designate the type of atomic defect in ceramics and their conc.

(iii) Stoichiometry:-

state of a ionic compound where exact ratio of cation-anions can be predicted by the chemical formula. Eg NaCl

(iv) Non-stoichiometry:-



state where exact ion type / state cannot be predicted e.g. Fe_xO_y

selection depends upon ambient O_2 pressure and temp.

Q. Describe Impurities in Ceramics

slide 24
imp

(i) Substitutional impurity (cation).

E.g. NaCl lattice having Na^+ cation is attacked by Ca^{+2} cation which would replace $2 \times \text{Na}^+$ ions with $1 \times \text{Ca}^{+2}$ ion and eventually leave a cation vacancy behind.

(ii) Substitutional impurity (anion)

Same concept of anion vacancy but with O^{-2} replacing $2 \times \text{Cl}^-$ ions.

describe the stress-strain behaviour of Ceramics.

The stress-strain behaviour of brittle ceramics is not usually ascertained by a tensile test for 3 reasons.

- (i) It is difficult to prepare and test specimens having the required geometry.
- (ii) It is difficult to grip brittle materials without fracturing them.
- (iii) Ceramics fail after only 0.1% strain, which necessitates that tensile specimens be perfectly aligned to avoid presence of bending stresses, which are not easily calculated.

→ flexural test

∴ a traverse bending test is most commonly used in which a rod specimen having either a circular O or □ cross section is bent until fracture three-to-four-point loading technique.

- (i) At the point of loading top surface of the specimen is at compression.
- (ii) Bottom surface is at tension.
- (iii) Stress is computed via "specimen thickness", "the bending moment", "moment of inertia".
- (iv) Max stress exist on the specimen directly below the loading point ↑

Note: Stress at the fracture using fractural test is called flexural strength. also

- (i) Modulus of rupture
- (ii) Fracture strength
- (iii) Bend.

Formula for fractural strength.

[here stress " σ " $\Rightarrow \frac{M}{I}$ \Rightarrow <sup>Max
bend
moment</sup> moment of inertia.]

(i) \square cross section.

$$\sigma_{fs} = \frac{3F_f L}{2bd^2}$$

b = length

d = width.

F = Load force

L = moment of Inertia.

(ii) \circ cross section.

$$\sigma_{fs} = \frac{F_f L}{\pi R^3}$$

R = Radius of specimen.

