

## NPTTEL COURSE

### ADVANCED CERAMICS FOR STRATEGIC APPLICATIONS

#### QUESTIONS AND ANSWERS

**Q1: What do you understand by "Ceramics"?**

**Ans:** Ceramics are a group of chemical compounds, either simple (consisting of only two different elements) or complex (consisting of more than two elements); possessing high (~ 1000°C) melting or decomposition temperature and consequently requiring high temperatures for their shaping. They are normally hard and brittle. Examples are: oxides, nitrides, carbides, oxynitrides, silicides, borides etc of different metals or metalloids.

**Q2: How do you distinguish between "Traditional" and "Advanced" ceramics?**

**Ans:** Traditional ceramics are naturally occurring clay based products e.g. products made of different types of porcelains, red clay bricks, terracotta product, refractories made of naturally occurring raw materials etc, where as advanced ceramics are normally made of high purity synthesized raw materials having exotic electrical, magnetic, optical, mechanical and thermo-mechanical properties. Examples are: barium titanate, Ni-Mn ferrite, lead-zirconate-titanate, lanthanum doped lead-titanate-zirconate (transparent), partially stabilized zirconia, silicon carbide, silicon nitride, titanium nitride, silicon-aluminium-oxynitride, aluminium-oxynitride, titanium-diboride, zirconium-diboride, etc.

**Q3: What is tri-axial porcelain? What are the different roles played by the different raw materials used in tri-axial porcelain?**

**Ans:** The name "tri-axial porcelain" comes from the three major naturally occurring raw materials used to manufacture the porcelain products. These are clay, quartz and feldspar. The roles played by these raw materials are as follows:

Clay – In presence of appropriate amount of water, it produces a plastic mass helping shaping of the product.

Quartz – It being a relatively high melting material provides the necessary mechanical strength to the final product and also helps retaining the shape during high temperature firing.

Feldspar – Being a low melting material and the product of melting being a viscous glassy liquid, it helps in binding all the solid particles present in the composition.

**Q4: Distinguish between "close" and "non-close" packed structures. Give a few examples of each.**

**Ans:** In a closed-packed structure all the atoms or ions are in the closest possible positions. In other words, all the atoms or ions are in contact with their neighbouring atoms or ions. In case such a condition is not satisfied, the structure is known as "non-close packed"

Examples: fcc, hcp, rocksalt, diamond, zinc blende, wurtzite etc are close packed structures.  
bcc, CsCl, rutile, fluorite etc. are non-close packed structures.

Q5: Show that the number of octahedral and tetrahedral interstitial sites available in a close packed structure is 1 and 2 respectively.

Ans: The best known example of a close packed structure is face centered cubic or fcc. In this structure, atoms are placed at all the 8 cube corners and 6 face centers.

It may be shown that the contribution of each of the corner atoms to the cube under reference is only  $1/8$  and that of the face centered atoms is  $1/2$ . So, the total number of atoms per unit cell of the fcc structure is  $1/8 \times 8 + 1/2 \times 6 = 4$ .

The octahedral interstitial sites are located at 12 edge centers and at the centre of the cube. The share of the edge center positions to the cube under reference is  $1/4$  and the one at the center of the cube contributes 1 octahedral site to the unit cell. So the total number of the octahedral site per unit cell is  $1/4 \times 12 + 1 = 4$ .

The tetrahedral sites on the other hand, are located on each of the 4 body diagonals at points having a the coordinates of  $(1/4, 1/4, 1/4)$  with reference to each of the corners of the cube. All of them are completely within the cube. There are in all 8 corners and corresponding to each corner there are one tetrahedral site. Therefore the number of tetrahedral sites is  $1 \times 8 = 8$ .

So the number of octahedral sites per atom is  $4/4 = 1$

And the number of tetrahedral site is  $8/4 = 2$ .

Q6: Calculate the theoretical lattice parameter of single MgO assuming that the ionic radii of  $Mg^{2+}$  and  $O^{2-}$  are 86pm (Pico meter) and 140pm respectively.

Ans: It is known that MgO crystallizes in cubic rock salt structure in which  $O^{2-}$  ions form the fcc structure and  $Mg^{2+}$  ions are placed in all the available octahedral sites. The cations and the anions touch each other along the cube edges, which is equal to a (where a is the lattice parameter).

$$a = 2(r_{Mg^{2+}} + r_{O^{2-}}) + 2(86 + 140) = 2 \times 226 = 452\text{pm}$$

Q7: If the atomic weights of Mg and oxygen are 24.3 and 16 respectively, what would be the theoretical density of MgO?

Ans: It is known that there are 4 molecules of MgO in a unit cell of MgO. Avagadro's No. is  $6.02 \times 10^{23}$ . Lattice parameter of the cubic unit cell is 452pm (from the previous exercise).

$$\begin{aligned} \text{So, } \rho &= \frac{4(24.3+16)}{6.02 \times 10^{23} \times (4.52 \times 10^{-10})^3} \text{ g/m}^3 \\ &= 2.89 \text{ g/cm}^3 \end{aligned}$$

Q8: What are the number of Ba, Ti and O ions in a unit cell of  $BaTiO_3$ ?

Ans: It is known that in a cubic  $BaTiO_3$  lattice, Ba ions occupy the corner positions, O ions are at the face centers and the cube center is occupied by the Ti ion.

So the number of Ba ions per unit cell is  $8 \times 1/8 = 1$

Number of O ions is  $6 \times 1/2 = 3$

and Ti ion being at the cube centre, it's number is 1.

**Q9:** The density of a hypothetical compound MX is  $2.05 \text{ g/cm}^3$ . It has a cubic structure with a lattice parameter of  $572 \text{ pm}$ . Atomic weights of M and X are 28 and 30.5 respectively. What may be its structure type?

**Ans:** Let us assume the ionic radii of M and X are  $r_M$  and  $r_X$ ; N is the number molecules per unit cell.

Molecular weight of the compound =  $28 + 30.5 = 58.5$

$$\text{So, density} = \frac{\text{Wt of one molecule} \times N}{\text{Volume of the unit cell}} = \frac{(58.5 \times N) / (6.02 \times 10^{23})}{(5.72 \times 10^{-8})^3} \text{ g/cm}^3$$

Or,  $2.05 = 0.52 N$

Therefore  $N = 2.05 / 0.52 \approx 4$

A few MX type compounds with different structure types known to us are NaCl, CsCl, Zinc Blende (ZnS) etc. Based on their atomic arrangement, both in NaCl and Zinc Blende structures the number of molecules per unit cell is 4 and therefore these are the possible structure types of MX in this case.

**Q10:** What do you mean by "isomorphous substitution" in silicate structures? Give two examples of the same.

**Ans:** As the ionic radius ratio of  $\text{Si}^{4+}$  to  $\text{O}^{2-}$  is very close to the critical radius ratio for a tetrahedral coordination the building block of any silicate structure is Si-O tetrahedron. On the other hand the radius ratio of  $\text{Al}^{3+}$  to  $\text{O}^{2-}$  is such that Al ion may have both tetrahedral and octahedral coordination. In several silicate structures a part of the  $\text{Si}^{4+}$  is substituted by  $\text{Al}^{3+}$  in the tetrahedral coordination and also substitution of octahedral  $\text{Al}^{3+}$  by other cations e.g.  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$ .

Such substitutions are normally referred to as "isomorphous substitution". As the substituted and substitution ions normally possess different charges, the charge difference is compensated by the presence of a third ion in the structure.

Examples:

Muscovite:  $\text{K Al}_2 (\text{OH})_2 (\text{AlSi}_3\text{O}_{10})$  - One out of 4  $\text{Si}^{4+}$  is substituted by  $\text{Al}^{3+}$ . Deficiency of the +ve charge is compensated by  $\text{K}^+$ .

Montmorillonite:  $(\text{Na,Ca})_{0.33} (\text{Al,Mg})_2 (\text{Si}_4\text{O}_{10})$  - One of the  $\text{Al}^{3+}$  is substituted by  $\text{Mg}^{2+}$ . Deficiency of the +ve charge is compensated partly by  $\text{Na}^+$  and partly by  $\text{Ca}^{2+}$ .

Q11: From the structural point of view, what is the commonality between pure silica, feldspar and anorthite? Please explain how the chemical formulae of the latter two compounds can be derived from the first.

Ans: The common feature is that all the clay minerals under reference possess the “framework” structure in which all the four silicon ions are shared between the neighbouring tetrahedral.

If we consider four formula units of  $\text{SiO}_2$  the formula can be written as  $\text{Si}_4\text{O}_8$ . If one of the four  $\text{Si}^{4+}$  ions is substituted by  $\text{Al}^{3+}$ , the formula becomes  $\text{AlSi}_3\text{O}_8$ . However, in order to maintain charge neutrality an additional cation in the form of  $\text{Na}^+$  is added to the structure resulting in the formation of Na-feldspar having the formula  $\text{NaAlSi}_3\text{O}_8$ .

In case of anorthite, 2 of the 4Si ions are substituted by Al and the consequent deficiency of 2 +ve charges is compensated by addition of one  $\text{Ca}^{2+}$  ion leading to the formula of anorthite as  $\text{CaAl}_2\text{Si}_2\text{O}_8$ .

Q12: What do you mean by “point defect”? Why are they named so?

Ans: Point defects are imperfections in the atomic/ ionic arrangement in a crystalline lattice. There may be different types of point defects e.g. vacancy, interstitial, impurity atom/ion present at regular lattice sites or at interstitial sites. In addition, there may be pair of point defects such as Schottky, Frenkel and Anti-Frenkel defects.

They are named as point defects because these defects are restricted to specific lattice points.

Q13: There is a strong correlation between point defects and non-stoichiometry; however, all types of point defect do not result in non-stoichiometry – Justify.

Ans: As per definition, non-stoichiometry means deviation from the law of constant proportion, according to which a specific ratio of cation to anion is required to be maintained in a chemical compound in order to maintain the charge neutrality. Presence of point defects (except the defect pairs) leads to deviation from this specific ratio resulting in non-stoichiometry.

However, formation of defect pairs such as Schottky and Frenkel pairs does not change the specific ratio of cation to anion and therefore does not lead to non-stoichiometry.

Q14: A non-stoichiometric oxide  $\text{Fe}_{1-y}\text{O}$  has a lattice parameter of 429pm and a density of 5.613g/cm<sup>3</sup>. Calculate the value of ‘y’ and also the density of defects (no. per unit volume).

Ans: It is known that FeO has a cubic (rock salt) structure.

So, the volume of the unit cell is  $(429\text{pm})^3 = (4.29 \times 10^{-8})^3 \text{ cm}^3 = 78.95 \times 10^{-24} \text{ cm}^3$

Each unit cell contains 4 molecules of FeO.

So, the mass of one unit cell = 4 x molecular wt of  $\text{Fe}_{1-x}\text{O}$  / Avagadro’s number

$$= 4\{(1-y) 55.8 + 16\} / (6.02 \times 10^{23} \text{ g})$$

$$\text{Density} = \frac{4 \times 55.8(1-y) + 64}{6.02 \times 10^{23} \times 78.95 \times 10^{-24}} = 5.613$$

$$\text{So, } 287.2 - 223.2y = 5.613 \times 6.02 \times 78.95 \times 10^{-1} = 266.6$$

$$\text{Therefore, } y = (287.2 - 266.6) / 223.2 = 0.093$$

$$\text{Number of Fe vacancies per unit cell} = 4 \times 0.093 = 0.372$$

$$\text{Volume of the unit cell as calculated above} = 78.95 \times 10^{-24} \text{ cm}^3$$

$$\text{Therefore n. of vacancies per unit volume} = 0.372 / 78.95 \times 10^{-24} = 4.71 \times 10^{21} / \text{cm}^3$$

Q15: Calculate the concentration of point defects in a solid at a temperature 1200°C if the enthalpy of formation of the defect is 150kJ/mol.

Ans: Expression to be used for the calculation is:

$$n/N = \exp(-\Delta H / 2kT)$$

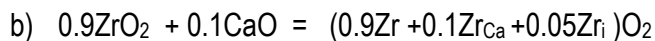
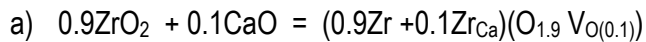
Here  $\Delta H$  is given in kJ/mol. For using the above equation one needs to convert the unit to eV.

$$150 \text{ kJ/mol} = 150000 / 96500 \text{ eV} = 1.554 \text{ eV}; k = 8.62 \times 10^{-5} \text{ eV/atom K}; T = 1200 + 273 = 1473 \text{ K}$$

$$\text{Therefore, } n/N = \exp(-1.554) / (2 \times 8.62 \times 10^{-5} \times 1473) = \exp(-6.12) = 2.2 \times 10^{-4}$$

Q16: Addition of CaO to ZrO<sub>2</sub> may give rise to the formation of two different types of point defects such as oxygen vacancy or Zr-interstitial. Calculate the densities of ZrO<sub>2</sub> – 10m/o CaO solid solutions assuming the two different forms of point defects mentioned above. Also assume that the lattice parameter remains constant at 515pm.

Ans: The defect reactions for the two situations are as follows:



It is also known that each cubic unit cell contains 4 molecules of ZrO<sub>2</sub> solid solution.

For the first case

$$\text{Mass of the unit cell} = 4(0.9 \times 91.2 + 0.1 \times 40 + 1.9 \times 16) / 6.02 \times 10^{23} = 77.4 \times 10^{-23} \text{ g}$$

$$\text{Volume of the unit cell} = (5.15 \times 10^{-8})^3 = 136.6 \times 10^{-24}$$

$$\text{Therefore density} = (77.4 \times 10^{-23}) / (136.6 \times 10^{-24}) \text{ g/cm}^3 = 5.666 \text{ g/cm}^3$$

For the second case

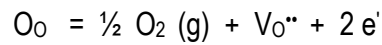
$$\text{Mass of the unit cell} = 4(0.9 \times 91.2 + 0.1 \times 40 + 0.05 \times 91.2 + 2 \times 16) / 6.02 \times 10^{23} = 81.49 \times 10^{-23} \text{ g}$$

$$\text{Volume of the unit cell} = (5.15 \times 10^{-8})^3 = 136.6 \times 10^{-24}$$

$$\text{Therefore density} = (81.49 \times 10^{-23}) / (136.6 \times 10^{-24}) \text{ g/cm}^3 = 5.965 \text{ g/cm}^3$$

Q17: Write the defect reaction for a typical oxygen deficient oxide with predominance of oxygen vacancy and show that the 'n' type conductivity is proportional to  $p_{O_2}^{-1/6}$ .

Ans: The defect reaction is



So, the equilibrium constant becomes

$$K = \frac{[V_{O''}] \cdot [e']^2 \cdot p_{O_2}^{1/2}}{[O_o] p_{O_2}^{1/2}}$$

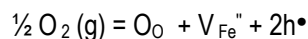
$$\text{Neutrality Condition: } 2 [V_{O''}] = [e'] = n$$

Therefore,

$$[e'] = n \propto p_{O_2}^{-1/6}$$

Q18: Write the defect reaction for a typical metal deficient oxide with predominance of metal vacancy and show that the 'p' type conductivity is proportional to  $p_{O_2}^{1/6}$ .

Ans: Considering that  $Fe_{1-x}O$  is a typical metal deficient oxide, one can write the defect reaction as



The equilibrium constant can be written as

$$K = \frac{[O_o] \cdot [V_{Fe''}] \cdot [h^\bullet]^2}{p_{O_2}^{1/2}}$$

$$\text{Neutrality Condition: } 2 [V_{Fe''}] = [h^\bullet] = p$$

Therefore

$$[h^\bullet] = p \propto p_{O_2}^{1/6}$$

Q19: Define 'dislocation'. What is its importance in understanding the properties of materials? How many types of dislocations are there and how do you differentiate them?

Ans: Dislocation is one dimensional or line defect created in a crystalline solid. It is defined as "A boundary between slipped and un-slipped portions of a crystalline solid lying on a slip plane". It is important for understanding the mechanical behavior, particularly the plastic deformation of a solid under a mechanical stress.

There are several types of dislocations. However, the two most important ones are: 1) edge and 2) screw dislocations. In case of the former the Burger's vector is perpendicular to the dislocation line, while for the latter, the Burger's vector is parallel to the dislocation line.

In addition to these two important varieties, there are partial dislocations and mixed dislocations, depending on the orientation of the dislocation line with respect to the Burger's vector.

Q20: Calculate the magnitude of the Burger's vector in an fcc lattice if its lattice parameter is 450pm. Also calculate the energy associated with the dislocation if the shear modulus of the crystal is 50GPa.

Ans: In an fcc lattice the slip plane (the closest packed plane) is (111) and the burger's vector is along the closest packed direction  $\langle 110 \rangle$  or in other words along the face diagonal. The magniyude of the vector is  $\frac{1}{2} \langle 110 \rangle$ .

Length of the face diagonal is  $\sqrt{2}(450)\text{pm} = 636.3\text{pm} = 6.363 \times 10^{-10}\text{m}$

Therefore the Burger's vector =  $\frac{1}{2} \times 6.363 \times 10^{-10} \text{ m} = 3.18 \times 10^{-10}\text{m}$

Energy associated with the dislocation is  $\frac{1}{2} Gb^2 = \frac{1}{2} \times 50 \times 10^9 (3.18)^2 \times 10^{-20} \text{ J} = 2.52 \times 10^{-9} \text{ J/m}$ .

Q21: Both grain boundary and twin boundary are two dimensional crystalline defects – Justify.

Ans: In a polycrystalline material, "grain boundary" is the internal boundary, which separates two neighbouring crystals (called grains) having different crystallographic orientations. So grain boundary is a kind of discontinuity in the atomic arrangement. It consists of a large concentration of dislocations and point defects. As the boundary surrounds a crystal or grain in the form of a surface, it is two-dimensional in nature.

A twin boundary arises from a cooperative and simultaneous movement of a set of atoms in a crystal, generating a plane of discontinuity in the orientation of the crystal and therefore it is also a two-dimensional planar defect

Unlike grain boundary, which is a curved surface, twin boundary is a planar surface.

Q22: Define electrical conductivity. Derive a generalized expression for electrical conductivity. What are the driving forces for electrical conduction in solids?

Ans: Electrical conduction is the result of charge transport through a medium. Two basic parameters, which characterize this phenomenon, are: the quantity of charge ( $q$ ) being and the velocity of its movement ( $v_d$ ). The conduction is normally induced by an externally applied electric field ( $E$ ).

According to Ohm's Law, the flux density (or current density) ( $j$ ) is proportional to the applied electric field ( $E$ ) and the proportionality constant is termed as the electrical conductivity ( $\sigma$ )

$$j = \sigma \cdot E$$

If  $z$  is the number of electronic charge ( $e$ ) with each of the mobile species and  $n$  is the number of charge carriers per unit volume or in other words the concentration of the charge carrier, the current flowing per unit cross section i.e. the current density ( $j$ ) may be expressed as

$$j = n \cdot z \cdot e \cdot v_d$$

Where,  $v_d$  is known as the drift velocity, which is the net velocity of the charged species in the direction of the applied field. Under certain considerations, it is also the average drift velocity between two consecutive collisions of the electronic charge with some barrier/ obstacles coming in the way of the movement of the species.

Applying Ohm's law  $\sigma \cdot E = n \cdot z \cdot e \cdot v_d$

So,  $\sigma = (n \cdot z \cdot e) (v_d/E) = n \cdot z \cdot e \cdot \mu$   
 where,  $\mu$  is the mobility of the charged species.  $= v_d / E$  and  $n$  is its concentration.

As mentioned above, the primary driving force for electrical conduction is the electric field particularly when the electron or electron hole is the charge carrying species. However, in case of ionic conduction, for which ions are the charge carrying species concentration gradient of the particular species may also act as the driving force for conduction, provided a parallel path is available for electronic charge transport.

**Q23: What do you mean by transference number? Provide an expression for the same in terms of conductivity.**

**Ans:** Particularly in ceramic materials having two or more ionic species, there may be more than one type of mobile charge carrier, which may contribute to the transport process under an applied electric field and therefore the general expression of conductivity is:

$$\sigma_T = \sigma_1 + \sigma_2 + \sigma_3 \dots \dots \sigma_n$$

In this context transference number ( $t_i$ ) refers to the fraction of total current carried by the specific charge carrier ( $i$ ) and is expressed as

$$t_i = \sigma_i / \sigma_T$$

where,  $\sigma_i$  is the partial conductivity arising from the conduction through the  $i$ th species and  $\sigma_T$  is the total conductivity arising from all the mobile species. Ceramic materials, ideally, may have four different kinds of charge carriers e.g. "free electron", "electronic hole", "cation" and "anion" and the summation of all the transference numbers becomes unity.

$$t_T = t_1 + t_2 + t_3 + t_4 = 1$$

where, the subscripts 1, 2, 3, 4 refer to the four different species mentioned above.

**Q24: What are the important theoretical models to explain the electrical phenomenon in solids? Discuss the basic assumptions and limitations of these models.**

**Ans:** There are three important theories put forward to explain the electrical conduction of different solids. These are:

1. **Ideal Gas Model for metals: In this model,**
  - a) The electron cloud is treated as an ideal inert gas and the energy of the individual electrons depends on the temperature and applied field.
  - b) In the absence of any electric field, electrons move with randomly distributed thermal velocities. However, in presence of the field, they acquire a net drift velocity, in the direction opposite to the field.
  - c) Unfortunately, this model cannot explain the temperature dependence of conductivity of metals. According to this model  $\sigma \propto \sqrt{T}$ . However, in reality  $\sigma \propto 1/T$
  - d) In order to resolve this issue, next model was proposed.



## 2. Free Electron Theory of Metals. In this model

- a) The electrons are assumed to have a constant but negative potential throughout the volume of the solid. However, the potential is very high at the edges of the solid and therefore the free electrons are normally bound within the volume of the solid.
- b) The model also takes care of the wave-particle duality of the free electrons.
- c) As per the Pauli exclusion principle electrons possess discrete (not continuous) energy levels,
- d) The phonons arising from the vibration of the atom cores act as the scattering centres for the free electrons giving rise to decreasing conductivity of metals with increasing temperature. ( $\sigma \propto 1/T$ ).
- e) However, this model does not explain the phenomenon of semiconductivity. In order to do that a third model namely Band Theory of Solids has been proposed.

## 3. Band Theory of Solids. In this model,

- a) It is assumed that the free electrons are not in a constant potential field, rather they experience a periodic potential.
- b) Based on the quantum mechanical approach it can be shown that the electronic energy levels are not even quasi-continuous, instead there are forbidden energy levels or in other words bands of energy levels separated by band gaps.
- c) This model finally explains the electrical behavior of three distinct groups of materials namely metals, semiconductors and insulators.

**Q25: Define "Band Gap" with reference to electronic energy levels in a solid. Distinguish between 'direct' and 'indirect' band gap. What do you mean by 'valance' and 'conduction' bands?**

- Ans:
- a) Referring to the parabolic E-k curve, the minimum energy gap considering all directions of motion is termed as the "Band Gap". If the maximum of the lower band for one direction of motion is higher than the minimum of the upper band for the same or any other direction of motion, then there is no forbidden gap. This is called overlapping band.
  - b) Such a situation happens if the potential energy of the electron is not a strong function of the position in the crystal.
  - c) If the highest energy in the lower band corresponds to the same value of k as that of the lowest value, the band gap is called direct band gap.
  - d) If these two energy levels are not on the same vertical line (same k value), then the gap is known as the 'indirect band gap'
  - e) At zero degree Kelvin the highest occupied band is known as the valence band and the next higher band is called the conduction band.