**I M.Sc CHEMISTRY**

**SEMESTER - IV**

**SOLID STATE CHEMISTRY (P16CHE1A)**

**2 MARKS**

**1) Define polymorphism .Give an example:**

When the temperature and pressure of a solid are changed , the internal arrangement of the atoms of the solid changes. The ability of a material to have more than one structure , in its solid state itself is called polymorphism.

**2) what are pseudo polymorphism? Give an example:**

Pseudo polymorphism can be defined into the different crystals type are the result of hydration or solvation.

**Examples:**

An example of an organic polymorph is glycine which is able to form monoclinic and hexagonal crystals.

**3) what are super molecular isomorphism?**

The word “isomorphism” applies when two complex structures can be mapped onto each other, in such a way that to each part of one structure there is a corresponding part in the other structure , where corresponding means that the 2 parts play similar roles in their respective structures.

**4) what do you meant by super molecular chemistry?**

Supra molecular chemistry refers to the domain of chemistry beyond that of molecules and focuses on the chemical systems made up of a discrete number of assembled molecular sub units or components.

(OR)

Super molecular chemistry can thus be regarded as involving a molecule (a host) binding another molecule (a guest)via non covalent binding or complexation.

Cram calls it ‘host-guest” chemistry while Lehn (1988) calls its “super molecular chemistry” which is the chemistry of non covalent intermolecular forces that bind 2 or more molecules leading to “super molecules”.

**5) what are molecular recognition &their types:**

It is defined by the energy and the information involved in the binding and selection of substrates by a given receptor molecule , it may also involve a specific function.

**Types:**

a) cation binding-spherical recognition

b) recognition of anionic substrates –anion binding-spherical and other anions.

c)tetrahedral recognition involving macro tricyclic cryptands

d) co receptor molecules and multiple recognition.

e) binding and recognition of neutral molecules.

**6) Define crystal engineering:**

Crystals engineering is the design and synthesis of molecular solid state structures with desired properties , based on an understanding and exploitation of intermolecular interactions. The two main strategies currently in use for crystal engineering are based on H – bonding and coordination complexation.

(or)

Crystal engineering may be defined as “ the understanding of intermolecular interactions in the context of crystal packing and the utilization of such understanding in the design of new solids with desired physical and chemical properties.

**7) What do you mean by non- covalent interaction?**

Non- covalent interaction also called non covalent forces (or) non-covalent bonds) are weak interactions between ions. Molecules and parts of molecules. A non-covalent bond is a type of chemical bond that does not involve the sharing of pairs if electrons but rather involves more dispersed variations of electromagnetic interactions. The non covalent bond is the dominant type of bond between super molecules in super molecular chemistry. There are 4 commonly mentioned types of non-covalent interactions.

1) hydrogen bonding

2) ionic bonding

3) vander walls force

4) hydrophobic interaction.

**8) What is a π-π interaction ? Give an example.**

π-π interaction are caused by inter molecular overlapping of p- orbitals in π- conjucated system, so they become stronger as the number of π-electrons increases.

The interaction which is a bit stronger than other non- covalent interaction ,play on important role in various parts of supra molecular chemistry.

In super molecular chemistry ,an aromatic interaction (or) π-π interaction is a non-covalent interaction between organic compounds containing aromatic moiety.

**9. What are NLO materials?**

Organic materials are expected to have relatively strong non linear optical properties due to delocalized electrons at π-π\* orbitals . This expectation explain extensive search for better NLO materials among organic crystals.

Ex : L- arginine maleate dihydrate (LAMD).

Organic NLO molecules posses donar-acceptor groups attached to an aromatic ring system that increases charge transfer through p- electron delocalization.

In polymer based NLO material the chromophore can be incorporated into a polymer material in a number of ways.

EX: L- arginine maleate dehydrate[LAMD]

**10) What are nano porous solids ? Give an example**.

A nano pore is a very small hole. It may for example be created by a pore forming protein or as a hole in synthetic material such as silicon graphene.

Nano porous materials, ( I .e) solids with pores of 0.5-5nm (corresponding to a few molecular diameters in width) are widely used in the chemical industry for the separation of gases and liquid catalysis and gas storage.

**11) Explain the design of molecular rods**:

Molecular rods are synthetical molecules consisting of a hydrophobic backbone and terminally varying functional groups have been synthesized for applications for functionalization of membranes.

Molecular rods designed for surface chairality studies have been synthesized in high yields.

**12) Explain the design of ladders and networks.**

**Ladders:** A ladders is a vertical or inclined set of rungs or steps. There are two types: rigid ladders that can be leaned against a vertical surface such as a wall and rope radders that are hung from the top.

**Networks:** A networks is a group of 2 (or) more computer systems linked together. Computers on a network are sometimes called modes.

**13). Write notes on OLED (or) How to prepare an OLED (or) What is an OLED?**

OLED is a flat light emitting technology made by placing a series of organic thin film between 2 conductors. When electrical current is applied, a bright light is emitted.

**14) What are the uses of OLED?**

1. OLED are used in television screens, computer monitors, small portable system screens such as mobile phones ,hand heldgames, watches.

2. They can also used in light sources for general space illumination and in large-area light -emitting elements.

3. A major area of research is the development of white OLED divices for use in solid- state lighting.

**15) What are the advantages of OLED vs LCD?**

OLED displays have the following advantages over LCD displays.

1. lower power consumption

2. faster refresh rate and better contrast

3. greater brightness

4. better durability

5. light weight

**16) Draw the diagram of OLED ?**

metal cathode Electron transport

layer

hole transport layer organic emitters

indium tin oxide anode glass substrate

**17 ) Write short notes on MOFs**

Metal organic frameworks are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-,two- (or) three- dimensional structures that can be porous.

**18) What are the uses of MoFs?**

1) MoF3 can be used for the storage of gases such as H2 and CO2

2) other possible applications of MoFs are in gas purification :

in gas separation in catalysis and a sensors.

**19) what are meta stable phases?**

Existences of a substance as either a liquid ,solid or vapour under conditions in which it is normally unstable in that state.

Many complex natural and man-made systems can demonstrate meta stability.

**20) What do you meant by zone melting?**

Zone melting is related to the stock berger method,but the thermal profile through the furnace is such that only a small of the charge is melted at any one time. Initially that part of the charge in contact with the seed crystal is melted. As the boat is pulled through the furnace, oriented solidification onto the seed occurs and at the same time more of the charge melts. This is also forms a well known method for the purification of solids, the zone refining technique.

**21) What is co precipitation precursor method?**

The reactants are mixed together , manually or mechanically in normal solid state reactions, and the subsequent reaction rate depends to a large degree on the particle size of the reactant, the degree of homogenization achieved. By using co precipitation procedures, it is sometimes possible to achieve a high degree of homogenization together with a small particle size and there by speed up the reaction rate.

**22) What Bridgman method?**

Bridgman method ,the melt is inside, a temperature, gradient furnace and the furnace is gradually cooled so that solidification begins at the cooler end. Bridgman method is used for the growth of single crystals .

**tm**

**T3 t2 t1 crystal**

**melt Original seed**

**23) What is solid state chemistry?**

Solid state chemistry, also sometimes referred to as materials chemistry ,is the study of the synthesis ,structure, and property of solid phase materials ,particularly, but not necessarily exclusively of non-molecular solids.

**24) Why are solid state reactions difficult?**

1) Solid state reactions takes place with great difficulty and only at high temperature .

2) The nucleation is rather difficult and this makes the solid state diffusion rates ,crystal orientation effects difficult.

**25) Define warger mechanism:**

The mechanism of reaction between MgO and Al2O3 described above ,involving the counter diffusion of Mg2+ and Al3+ ions through the product layer followed by further reaction at 2 reactant-product interface is known as the warner mechanism.

Interface MgO/ Mg Al2O4

2 Al3+ - 3Mg2+**+** 4 MgO MgAl2O4

Interface MgAl2O4/ Al2O3 :

3Mg2+ - 2 Al3+ + 4Al2O3 3MgAl2O4

Overall reaction:

4 MgO + 4Al2O3 4Mg Al2O4

**26) What is meant by kirkendall effect?**

The interface between reactant and product can be cleavly seen perhaps due to a difference in colour, the movement of the interface may be used as a marker to monitor the progress of the reaction. This effect of using a marker is known as the kirkendall effect.

Interface MgO/ MgFe2O4 :

2 Fe3+ - 3Mg2+**+** 4 MgO Mg Fe2O4

Interface MgFe2O4/ Fe2O3 :

3Mg2+ - 2 Fe3+ + 4Fe2O3 3MgFe2O4

Overall reaction:

4 MgO + 4Fe2O3 4Mg Fe2O4

**27) What are topotatic and epitatic reaction?**

Epitatic reaction require only a two- dimentional structural similarly at the crystal interface.

Epitatic reaction are more specific than epitatic ones because they require not only the structural similarity at the interface. But also that this similarity should continue into the bulk of both crystalline phase.

Epitatic means three- dimentional relationship between seed and crystal.

**28) Write a short notes on zeolite synthesis?**

The starting materials for zeolite synthesis may be aqueous solution of silicate and aluminate anions. Which are mixed together with alkali. A gel forms by a process of co polymerization of the silicate an aluminate anions. And on subsequent heat treatment, perhaps under a hydro –thermal treatment, crystal of zeolite are produced.

Aq.NaAl(OH)4 + aq.Na2SiO3 +aq. NaOH

25°C, copolymerisation

(Naa(AlO2)b (SiO2)c .NaOH. H2O) gel

25-175°C

(Nax(AlO2)x(SiO2)y). mH2O

Zeolite crystal

**29) What are the conditions involved in zeolite synthesis?**

1) reactive starting materials should be used . such as freshly co precipitated gels.

2) relatively high pH, introduced in the form of an alkali metal hydroxide or other strong base.

3) low temperature hydro thermal conditions with concurrent low autogeneous pressure at saturated water vapour pressure are needed.

4) a high degree of super saturation of the components of the gel is desirable leading to the nucleation of a large number of crystals.

**30) Define melts & gels, glasses?**

**Melts :**

Melts are high temperature liquids whereas aqueous solution are liquids at low temperature crystallization of melts is a valuable method for growing single crystals.

**Gels (or) solution:**

Zeolite synthesis

**Glasses:**

Glasses are sometimes useful to prepare crystalline material via intermediates: an important applications is in the manufacture of glass-ceramic materials.

LiO2 + SiO2 Cooled at room temp Li2Si2O5

**1 : 1** 1100°C( few hours)

**31) What is meant by van- arkel method?**

The van- arkel method for the purification of certain metals makes use of an exothermic reaction between metal and iodide to form a gaseous iodide.

Ex: Cr +I2 CrI2 (g)

Other metals which may be purified by this method include Ti,Hf,V,Nb,Cu,Ta,Fe,Th.

**32) What are graphite intercalation compounds? Give an example.**

Graphite has a planar ring structure and it is the classic example of a host crystal that is capable of intercalating a wide variety of atoms,ions and molecules.

**Example:**

1) graphite fluoride

2) CsK

3) graphite/ FeCl3

4) CsBr

**33) What do you meant by ion exchange reaction?**

Ion exchange is an exchange of ions between two electrolytes or between an electrolytic solution and a complex. In most cases the term is used to denote the process of purification,separation and decontamination of aqueous and other ion-containing solution with solid polymeric and mineralic “ion exchanges”

**34) Explain about the word of “ chimie douce”**

The precursor methods have the advantages that reaction takes place of much lower temperature then when using normal solid state reaction procedures. Another use of precursor method is in the synthesis of new metastable phases which cannot be prepared by other routes. The French have coined the delightful term “chimie douce” for this preparative method.

**35) How do prepare thin films?**

Various methods are used to prepare thin films .one method is given below:

**Cathodic deposition:-**

This is standard method for electro plating 2 metal electrodes are dipped into an application of an external field across the electrodes. Metal ions form the solution are deposited on the cathodes as a thin films. In order to maintain charge balance, the anodic metal gradually dissolve in the electrolyte.

**36) What are the advantage & disadvantage of melt growth & solution growth methods?**

|  |  |  |
| --- | --- | --- |
| **METHOD** | **ADVANTAGE** | **DISADVANTAGE** |

**Melt growth:** Rapid growth rates, crystal quality may be

Czochralski, giving layer crystals, poor with inhomogenitie

Bridgman, stock barger, simple apparatus. -s and large defent conc

verneuil -entration.

**Solution growth: isothermal conditions slow growth rates;**

Water crystallisati with slow growth rates problem of contamination

-on, flux growth, give quality crystals of by container or flux.

Hydrothermal method low defect concentration

|  |
| --- |
|  |

**37) what are the uses of hydro thermal method?**

1) hydro thermal method is used to synthesis of new phases like calcium silicate hydrates and to growth of single crystals.

2) using this method many substances have been prepared as high quality single eg: corundum (Al2O3) and ruby (Al2O3 dipped with Cr3+)

**38) what are spinels? Give an example ?**

Spinel is the magnesium aluminium number of the larger spinel group of minerals. It has the formula MgAl2O4.

Spinel is found as a metamorphic mineral in rare mafic igneous rocks. In these igneous rocks the magmas are relatively deficient in alkali’s relative to aluminium oxide may form as the mineral corundum or may combine with magnesium to form spinel.

**39) what are antistokes phosphors?**

Antistokes phosphors exhibit the remarkable property of emitting light or photons of higher energy (shorter wavelength) than the incident exciting radiation.

**Example:**

Antistokes phosphors convert infrared radiation into higher energy visible light.

39**) define ferromagnetism?**

If the interaction among the permanent dipoles is strong such that all the dipoles line up in parallel, the materials is ferromagnetic.

**40) what do you meant by anti ferromagnetism?**

If the permanent dipoles line up in antiparallel direction, and are equal the material is antiferromagnetism and the magnetization vanishes.

**41) what is meant by an eddy current?**

An additional source of energy loss in alternating magnetic field is associated with electrical currents called eddy currents, that are induced in the materials.

**42) what are ferrimagnetism?**

If the magnitudes of permanent dipoles aligned antiparallel are not equal. Thus exhibiting magnetization then the material is ferromagnetic, such an uncompensated antiferromagnetism is known as ferrimagnetism.

**43) define neel temperature & curie temperature ?**

**Neel temperature:**

The temperature above which an anti ferromagnetic substance loses its anti ferromagnetism and becomes paramagnetic.

**Curie temperature:**

The temperature above which a ferro magnetic substance loses its ferromagnetism and becomes paramagnetic.

(or)

Curie temperature is the certain temperature for a magnet at what it loses its magnetic energy completely.

**44) what are the methods used to study about the transition metal oxides?**

1) x-ray powder diffraction pattern

2) neutron powder diffraction pattern

**45) what are the types of spinels? Give an example:**

1) normal spinel [A] tet [B2]oct O4.

**Example;** (znFe2O4)MgAl2O4)

Inverse spinel[B]tet [A,B]octO4.

**Example;** (MgFe2O4)Mg2TiO4

**46. What do you meant by garnets? Give an example.**

The garnets are a large family of complex oxides , some of which are important ferromagnetic materials. They have the general formula A3B2X3O12.

Ais a larger ion.

B and X are smaller ions.

**47. What are the applications of magnetic materials?**

a. Transformer cores: High resistivity and negligibly small eddy currents.

b. Information storage: Information storage are essential components to modern computer technology.

c. Magnetic bubble memory devices: These magnetic bubble materials can be used as memory components for binary digital computers.

d. Permanent magnets: It increases the remanent magnetization of the material.

**48.What are luminescence and their types?**

Emission of radiation from a matter when it is supplied with some form of energy is called luminescence.

**Types:**

1. **Photoluminescence:** if the excitation is by the absorption of photons then it called photoluminescence.

2**.Cathodoluminescence:** if it is by bombardment with a beam of electrons then it is called cathodoluminescence.

**49. What are fluorescence?**

If the luminescence persists for a period less than or equal to the lifetime of the transition between the energy levels (10-8 sec) then it is known as fluorescence.

**50. What are phosphorescence?**

If the luminescence persists for much longer time than the life time of the transition , then it is called phosphorescence.

Materials exhibiting phosphorescence are known as phosphors.

The presence of impurity ions within the material give rise to traps leading to phosphorescence. These impurity ions are called activators.

**51. What is meant by sensitizer?**

It is defined as a molecule unable to absorbs the light radiation itself, hence there is another molecule required to absorb light. It gives the absorbed energy to the reactant molecule, such molecule is called sensitizer.

**52. What is meant by stokes shift ?**

In luminescent materials energy is transferred to the crystals by the absorption of a photon by the activator ion itself. The same energy levels are involved in both absorption and emission. Hence the absorbance and emission. Hence the absorption and emission wavelength are expected to be identical. But the emission peak is red shifted compared to the absorption peak. This phenomenon is known as stokes shift.

(or)

When the emission peak from a material is red shifted compared to its is called stokes shift.

**53) what do you meant by non- radio active energy transfer?**

Non-radio active energy transfer means transfer of energy to neighbouring activatorn ions,with little or no loss of energy during transfer, and at the same time the sensitizer ions return to their ground state. Finally the activator ions return to their ground state by the emission of luminescent radiation.

**54) give some examples of phosphor material?**

a) A phosphor that is used extensively in fluorescent lamps in an apatite, doubly doped with Mn2+ and Sb3+

b) Zn2SiO4(willemite) green colour

c)Y2O3 red colour

d)CaMg(SiO3)2 (diopside) blue

**55) define lasers, and their uses?**

A laser is a source of mono chromatic radiation available principally in the visible and infra red regions. The name laser stands for light amplification by stimulated emission of radiation.

**USES:**

The laser is used in holography, radio communication in outer space,piercing holes at great distance, welding, surveying and delicate surgery.

**56) what are the types of lasers?**

Many types of laser system have been discovered. The commercially available ones fall into three main categories.

**They are**

1) gas lasers

2)dye lasers

3) solid state lasers

**57) what is meant by phosphors?**

Materials exhibiting phosphorescence are known as phosphors.The presence of impurity ions within the material give rise to traphs feading to phosphorescence. These impurity ions are called activators.

**58) Define high Tc superconductors?**

In general when the superconducting transition temperature is above the boiling point of liq. Nitrogen (TTK) then material is called high Tc superconductors.

**59) Define super conductivity?**

Certain metals and alloys exhibit almost zero electrical resistivity. When they are cooled to sufficiently low temperatures. This phenomenon is known as super conductivity.

**60) what are perovskite? Give an example?**

Perovskite are named after the minerals CaTiO3,identified by the Russian mineralogist perovski. These oxides are having the formula unit of ABO3. The structure is formed by the cubic close packing of A atoms (bigger) at the corners and oxygen atoms at the face centers and B atoms (smaller) at the body center. In this structure the bigger cation is “12” co- ordinated and the smaller cation is “6” co-ordinated.

example:

NaNbO3, BaTiO3,CaZrO3, SrTiO3 .

**61) what are the applications of phosphors?**

Phosphors are important constituents of energy efficient fluroscent lamps, cathode ray tubes used in televisions, oscillo scopes,and displays and in x-ray detectors used in diagnostic equipment.

**62) Define asymetric synthesis:**

The production of an optically active compound from a symmetric molecule without the necessity of resolution is called asymmetric synthesis.

**63)write structures of α,β-form of 0-ethoxy –trans cinnamic acid ?**

**α-from: COOH**

**[ head-tail formation]**

HOOC

Truxillic acid

Β- form: COOH

[head-head formation]

COOH truxinic acid

**64) what do you mean by conformational effect?**

Most organic molecules in liquid and gaseous states are flexible and can change their shape. These molecules can readily flip from one form to the other since no bands are broken in the process; such effects are known as conformational effects.

**65) write about photo polymerisation of diacetylenes:**

The acetylinic molecules contain 2 reactive centres. In the crystalline state, they are arranged schematically, each being displaced laterlly relative to its neighbours. On UV irradiation, the stereo regular polymer results.

**R** **R**

**R R hγ ∫ ∫**

**R R**

**66)How to prepare an electrically conducting polymer (or) organic metal ?**

**First method:**

Acetylene is bubbled through a solution of the catalyst and a solid poly acetylene precipitate forms.

**Second method:**

Acetylene gas is introduced into a glass tube whose inner surface is coated with a thin layer of catalyst: a layer of poly acetylene forms on the surface of the catalyst.

**67) what are the application of doped poly acetylene?**

1) Doped poly acetylene has high electronic conductivity.so it is used to fabricate the P-N diode junctions.

2) doped poly ecetylene may be used as reversible electrodes in new types of battery.

3) doped poly ecetylene behave as a mixed ionic-electronic conductor.

**68) define polypyrrole:**

Pyrrole can be polymerized to give a long chain structure which effectively has alternate double bonds. Polypyrrole itself has a low conductivity but it can be oxidized by perchlorate to give P-type conductivity as high as 102 ohm-1cm-1

H

N

**∫**

**N N**

**H**

**NC CN Cl cl**

N N

NC CN

**STRONG π ELECTRON ACCEPTOR**