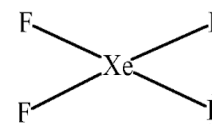
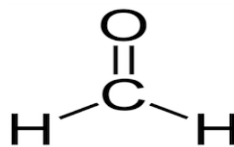
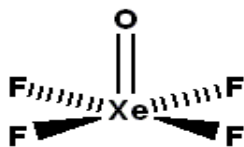
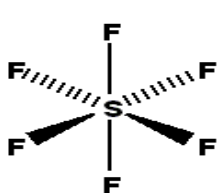
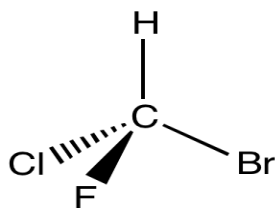


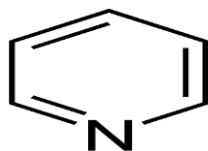
**Q1:**



1.  $E, C_2^4, C_1^4, 4C_2, \sigma_h, 2\sigma_v, 2\sigma_d$     $E, C_2^4, C_1^4, 4C_2, 4\sigma_v$     $E, C_2^3, C_1^3, 2\sigma$     $E, C_2^4, C_1^4, 4C_2, \sigma_h, 2\sigma_v, 2\sigma_d$



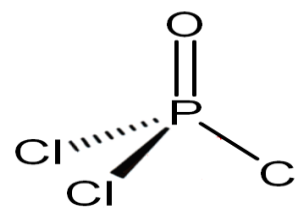
E



$E, C_1^2, 3\sigma_v$



$E, C_2^3, C_1^3, 3C_2, \sigma_h, 3\sigma_v$



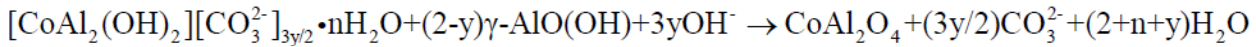
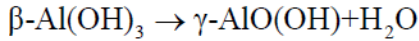
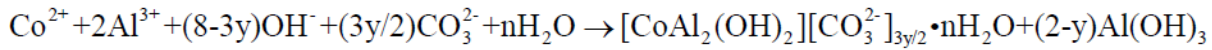
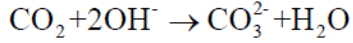
$E, C_2^3, C_1^3, 3C_2, 3\sigma_v$

**Qu.2:**

A. Write short notes on hydrothermal method and explain your answer with example.

Hydrothermal synthesis is a process that utilizes single or heterogeneous phase reactions in aqueous media at elevated temperature and pressure to crystallize anhydrous ceramic materials directly from solutions. Hydrothermal techniques are widely used in industrial processes for the dissolution of bauxite and for the preparation of aluminosilicate zeolites. This synthesis offers a low-temperature, direct route to oxide powders with a narrow size distribution avoiding the calcination step. Additional merits of this technology are attributed to the low costs for instrumentation, energy and precursors. Recently this method has been exploited for the synthesis of nanocrystalline oxide powders, such as zinc aluminate. Basically, the mechanism of hydrothermal reactions follows a liquid nucleation model. Detailed principles are comprised of theories of chemical equilibrium, chemical kinetics and thermodynamic properties of aqueous systems under hydrothermal conditions. However, in the supercritical region of water, little data are available at present, except those for pure water and simple salt-water solutions. Thus, a complete mechanism still has not been well founded and present studies contain a lot of inconsistencies.

Furthermore, in various cases, hydrothermal mechanisms are different from one another. For example, in  $\text{CoAl}_2\text{O}_4$  and  $\text{ZnAl}_2\text{O}_4$  preparation, Z. Chen *et al.* proposed that the final product precipitated from precursors, Layered Double Hydroxides (LDHs), with the formula  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2] \cdot [\text{A}^{m-}]_{x/m} \cdot n\text{H}_2\text{O}$ . A series of chemical reactions are expressed as following:



In the case of  $\text{BaTiO}_3$ , different mechanisms can be grouped either as in-situ transformation or as dissolution-precipitation, all of which being based on the more general nucleation-growth process. In a very detailed study, an in-situ mechanism involves either reactions of barium at the surface of the titania particles to form an inwardly growing shell of barium titanate, or the diffusion of barium ions within the amorphous titania, followed by dehydration, rearrangement of the titania network and finally the nucleation of barium titanate. The dissolution-precipitation mechanism has been suggested by Ovrmenko *et al.* and recently by Eckert. In fact, these last authors observe that the mechanism evolves from a dissolution-precipitation process at the beginning of the reaction to an in-situ mechanism for longer reaction times. Applied to ceramic powders, the process involves heating metal salts, oxides or hydroxides as a solution or suspension in a liquid at controlled temperature and pressure for about 20 hr. Typically the temperature in a hydrothermal process falls between the boiling point of water and the critical temperature ( $T_c = 374^\circ\text{C}$ ), while the pressure is over 100 kPa. The product is washed by de-ionized water to get rid of ions in the solvent and other impurities. After drying in air, fairly well-dispersible ceramic nanoparticles are obtained. For instance, to prepare  $\text{ZnAl}_2\text{O}_4$ , we could start with  $\text{ZnCl}_2$  and  $\text{AlCl}_3$ , in  $\text{NaOH}$  solution while  $\text{Ba}(\text{OH})_2$  and  $\alpha\text{-FeOOH}$  are used to prepare  $\text{BaFe}_{12}\text{O}_{19}$ .

**B.** Calculate the wavelength (nm) of the following:

1.  $E = hc/\lambda = 994 \text{ nm}$

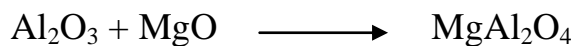
2.  $\lambda = h/(2\text{mev})^{1/2} = 0.00797 \text{ nm}$

Q3:

### 1. Ceramic method

It is one of the oldest, simplest methods which used in the preparation of inorganic materials. It depends on the reaction between the reactants in solid state for long time under high certain temperature and for example as the following:

The synthesis of magnesium aluminate from aluminum oxide and magnesium oxide at 1400°C for 12 hour.



#### The factor affects the method:

1. Particle size
2. Grinding time
3. Nature of reactants
4. Temperature
5. Time

#### Advantage of the method:

Simple method, Easy method, Low contamination, low pollution

#### Disadvantage of the method:

It needs to high temperature, long time, high particle size and two phase production.

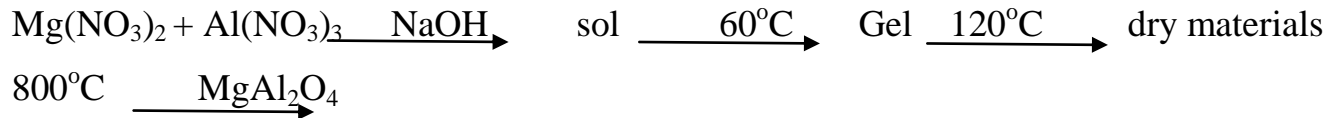
B. Mention the applications of optical and electron microscopes with explain only two

1. Study and determine the particle size and shape
2. Study the texture and surface details of materials
3. The study of crystal defects in the crystal of different materials
4. Chemical analysis
5. Structure determination
6. The study of precipitation and phase transitions in materials

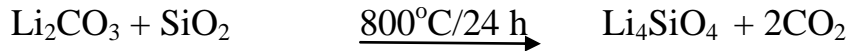
Q4:

A.

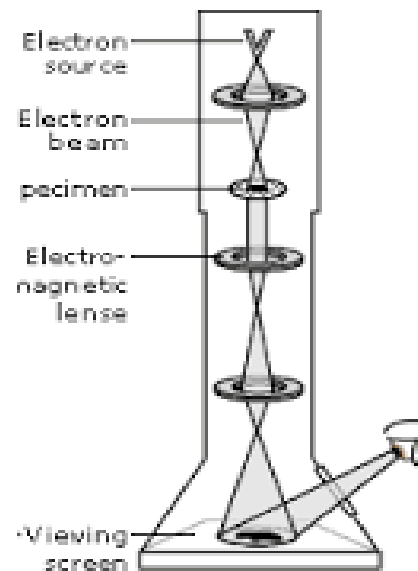
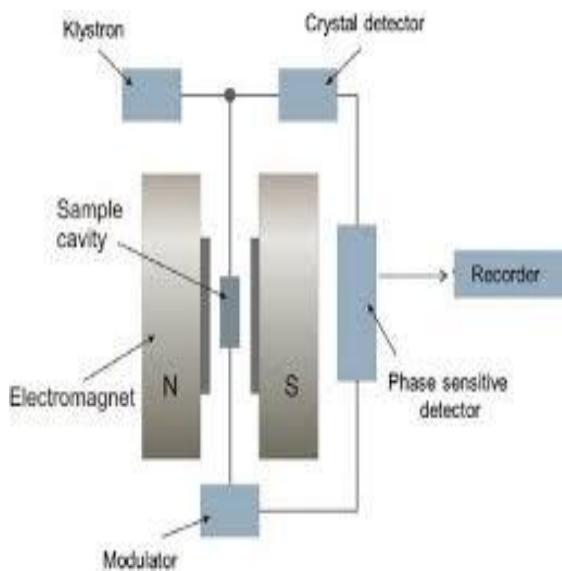
1.  $\text{MgAl}_2\text{O}_4$  is used as white ceramic pigment and can be prepared by sol gel method as the following:



2.  $\text{Li}_4\text{SiO}_4$  prepared using ceramic method from oxides at  $800\text{-}900^\circ\text{C}$  and using as conductor material



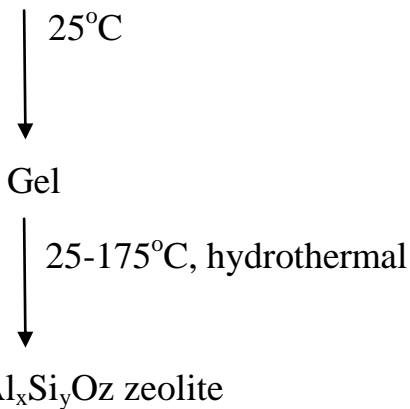
B.



Q5

A. The sol-gel process may be the most widely used and developed one among various synthetic powder preparation methods. The sol-gel method offers specific advantages in preparations of multi-component oxide ceramics. The early formation of a gel provides a high degree of homogeneity and reduces the need of atomic diffusion during the solid-state calcinations. Moreover, the processing often starts with metal alkoxides, many of which are liquids or volatile solids that can easily be purified, providing extremely pure oxide precursors. This factor is important for electroceramics synthesis. However, the relative high costs of the metal alkoxides may be prohibitive for certain applications, and the release of large amounts of alcohol during the calcination step requires special safety considerations. In sol-gel

preparation, a solution of the appropriate precursors (metal salts or metal organic compounds) is formed first, followed by conversion into homogeneous oxide networks (gel) after hydrolysis and condensation. Drying and subsequent calcination of the gel yields an oxide product. Usually, for preparation of multi-component oxides, alkoxides are mixed together in alcohol. Components for which no alkoxides are available are introduced as salts, such as acetates. Hydrolysis is carried out under controlled temperature, PH and concentration of alkoxides, added water and alcohol. Hydrolysis and condensation to polymeric species are represented by the following reaction equations (use alkoxides as an example): Metal oxygen metal (M -O- M) bonds are formed in solution by self-condensation or by cross-condensation when different alkoxides are used. After calcination, the organic group, R, is removed, leaving metal oxides. If the sol-gel process is carried out with a mixture of alkoxides with different hydrolysis and condensation rates, the molecular homogeneity in the initial stage can thus be lost during hydrolysis. The hydrolysis rate, which can be adjusted by the selection of OR ligands and reaction conditions, affects particle formation, growth and aggregation. Subsequent drying steps also influence the purity and morphology of the final product. There are several types of synthetic zeolites that form by a process of slow crystallization of a silica-alumina gel in the presence of alkalis and organic templates. One of the important processes used to carry out zeolite synthesis is sol-gel processing. The product properties depend on reaction mixture composition, pH of the system, operating temperature, pre-reaction 'seeding' time, reaction time as well as the templates used (alkylammonium cation). In sol-gel process, other elements (metals, metal oxides) can be easily incorporated. The silicate sol formed by the hydrothermal method is very stable. The ease of scaling up this process makes it a favorite route for zeolite synthesis. The calcination of materials at 300-400oC to remove the templete



$$g_s = g_{st} \times B_{st} / B_s$$

$$B_{st} = 3330 \text{ G}, g_{st} = 2.0028, g_{s(1)} = 3220 \text{ G}, g_{s(2)} = 3245 \text{ G} \text{ and } g_{s(3)} = 3270 \text{ G}$$

$$1. g(1) = 2.07122$$

$$1. g(2) = 2.05526$$

$$2. g(3) = 2.03955$$

$$a = 25 \text{ G}$$

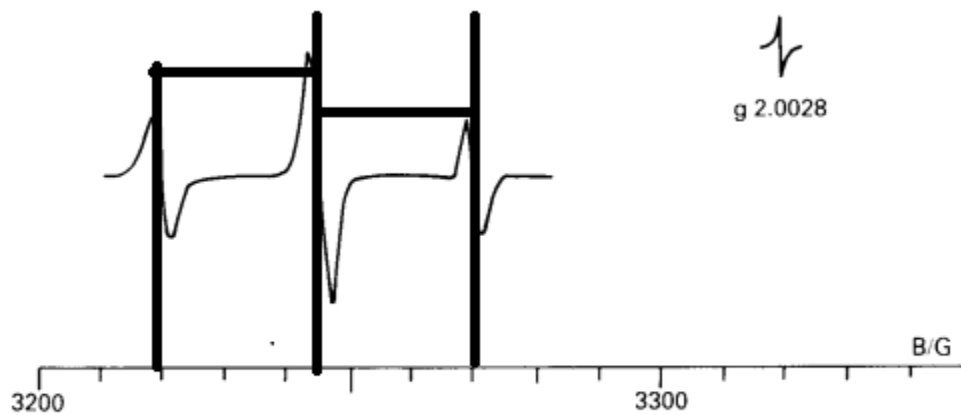
$$n. \text{ of lines} = 2nI + 1 = 3 = 2 \times 3 \times I + 1$$

$$6I = 2 \quad I = 1/3$$

$$E = g\mu B = 3220 \times 2.07122 \times 9.723 \times 10^{-12} \text{ J/G} = 6.485 \times 10^{-8} \text{ J}$$

$$E = g\mu B = 3245 \times 2.05526 \times 9.723 \times 10^{-12} \text{ J/G} = 6.485 \times 10^{-8} \text{ J}$$

$$E = g\mu B = 3270 \times 3270 \times 9.723 \times 10^{-12} \text{ J/G} = 6.485 \times 10^{-8} \text{ J}$$



Q6:

**Mention the applications of electron microscopy with explain only one:**

1. Study and determine the particle size and shape
2. Study the texture and surface details of materials
3. The study of crystal defects in the crystal of different materials
4. Chemical analysis
5. Structure determination
6. The study of precipitation and phase transitions in materials

**B.** Explain how you can refine chromium metal using vapor phase transport method.

VAPOR PHASE TRANSPORT VPC MATERIALS SYNTHESIS, CRYSTAL GROWTH, PURIFICATION

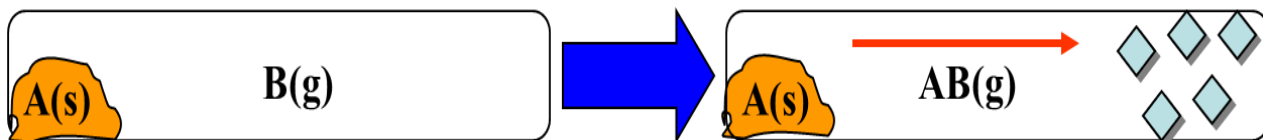
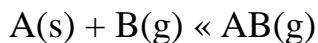
Sealed glass tube reactors

Reactant(s) A

Gaseous transporting agent B

Temperature gradient furnace DT ~ 50oC

Equilibrium established



Temperature dependent K

Equilibrium concentration of AB(s) changes with T

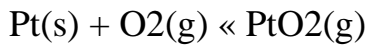
Different at T2 and T1

Concentration gradient of AB(g) provides thermodynamic driving force for gaseous diffusion from T2 to T1

It is used in synthesis of new solid state materials, growth of single crystals, purification of solids

Purification of Metals

Van Arkel Method



Exothermic, PtO<sub>2</sub> (g) forms at T1, pure Pt(s) deposited at T2

Useful for Ti, Hf, V, Nb, Cu, Ta, Fe, Th

Removes PtO<sub>2</sub> forms at hot end

Diffuses to cool end

Deposits well formed Pt crystals

Observed in furnaces containing Pt heating elements

CVT, T<sub>2</sub> > T<sub>1</sub>, provides concentration gradient and free energy thermodynamic driving force for gaseous diffusion of vapor phase transport agent PtO<sub>2</sub> metals from carbide, nitride, boride, silicide, oxide impurities!!!

Calculate the number of lines appear in ESR spectrum for the following species: [M (I=3/2), V(I<sub>V</sub>=7/2), Cr (I<sub>Cr</sub>=3/2), C (I=0) and H (I=1/2)]

1. CH<sub>3</sub>

2. M

3. C<sub>6</sub>H<sub>6</sub>

4. MH

5. MH<sub>2</sub>

6. MH<sub>3</sub>

7. [VO]<sup>2+</sup> complex

8. CrO<sub>4</sub><sup>3-</sup>

CH<sub>3</sub>, n. of lines equal to four

n. of lines equal to one

Total n. of lines equal to five



MH<sub>3</sub>. of lines equal to one

n. of lines equal to four

Total n. of lines equal to five

[VO]<sup>2+</sup>. of lines equal to eight

Total n. of lines equal to one

Total n. of lines equal to nine

CrO<sub>4</sub><sup>3-</sup>. of lines equal to four

n. of lines equal to one

Total n. of lines equal to five

MH<sub>2</sub> of lines equal to four

n. of lines equal to three

Total n. of lines equal to seven

C<sub>6</sub>H<sub>6</sub> of lines equal to six

n. of lines equal to one

Total n. of lines equal to seven

MH of lines equal to four

n. of lines equal to two

Total n. of lines equal to five

M of lines equal to four

