Q1

A.

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^{o}C for 12 hour.

$$Al_2O_3 + MgO \longrightarrow MgAl_2O_4$$

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.

2. **Hydrothermal synthesis**

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 for 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 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 $CoAl_2O_4$ and $ZnAl_2O_4$ preparation, Z. Chen *et al.* proposed that the final product precipitated from precursors, Layered Double Hydroxides (LDHs), with the formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]\cdot[A^{m-}]_{x/m}.nH_2O$. A series of chemical reactions are expressed as following:

$$CO_2+2OH^- \rightarrow CO_3^{2-}+H_2O$$

$$Co^{2+}+2Al^{3+}+(8\text{-}3y)OH^-+(3y/2)CO_3^{2-}+nH_2O \rightarrow [CoAl_2(OH)_2][CO_3^{2-}]_{3y/2}\bullet nH_2O+(2\text{-}y)Al(OH)_3$$

$$\beta\text{-}Al(OH)_3 \rightarrow \gamma\text{-}AlO(OH)+H_2O$$

$$[CoAl_2(OH)_2][CO_3^{2-}]_{3y/2}\bullet nH_2O+(2\text{-}y)\gamma\text{-}AlO(OH)+3yOH^- \rightarrow CoAl_2O_4+(3y/2)CO_3^{2-}+(2+n+y)H_2O$$

In the case of $BaTiO_3$, 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 Ovramenko 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 (Tc = 374°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 $ZnAl_2O_4$, we could start with $ZnCl_2$ and $AlCl_3$, in NaOH solution while $Ba(OH)_2$ and α-FeOOH are used to prepare $BaFe_{12}O_{19}$.

B. Compare between optical and electron microscopes (Source, Lens, Sample, Magnification, Resolution).

	optical microscopy	electron microscopy
Source	light	electrons
Lens	glass	Electron magnetic wave
Sample	Depend on the type	Depend on the type
Magnification	1500-60000X	Millon X
Resolution	0.3-0.7 µm	0.0001 µm
price	Not expensive	expensive
energy	$E=hc/\lambda$	$E=h/(2mev)^{1/2}$

C. 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

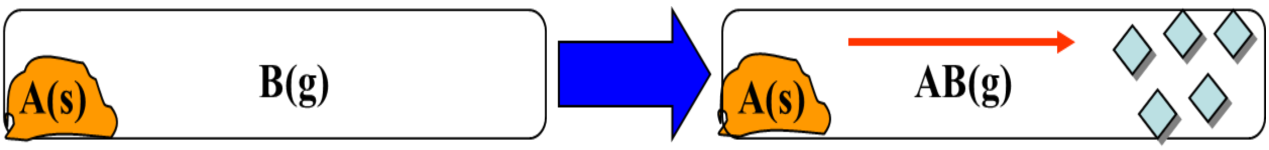
Reactant(s) A

Gaseous transporting agent B

Temperature gradient furnace DT ~ 50oC

Equilibrium established

A(s) + B(g) « AB(g)



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

Cr(s) + I2(g) (T2) « (T1) CrI2(g)

Exothermic, CrI2(g) forms at T1, pure Cr(s) deposited at T2

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

Removes metals from carbide, nitride, boride, silicide, oxide impurities!!!

D. Calculate the number of lines appear in ESR spectrum for CH3 (IH=1/2), MH3 (IM= 0), [VO]2+ complex (IV=7/2) and CrO43- (ICr=3/2).

CH_3 , n. of lines equal to four

n. of lines equal to one

Total n. of lines equal to five

MH_3. of lines equal to one

n. of lines equal to four

Total n. of lines equal to five

$[VO]^{2+}$. of lines equal to eight

Total n. of lines equal to one

Total n. of lines equal to nine

CrO_4^{3} . of lines equal to four

n. of lines equal to one

Total n. of lines equal to five

Q2:

A.

1. E
2. E, C^2_4, C^1_4, $4C_2$, σ_h, 2σv, 2σd
3. E, $C^2$3, $C^1$3, 3C2, 3σv
4. E, C^2_4, C^1_4, $4C_2$, σ_h, 2σv, 2σd

B.

1. $YBa_2Cu_3O_7$:

$YBa_2Cu_3O_7$ prepared using ceramic method from oxides at 930 °C and cooling gradually to 350°C in the presence of O_2. It si used as superconductor materials

$$Y_2O_3 + 4\,BaO + 6\,CuO + \tfrac{1}{2}\,O_2 \longrightarrow YBa_2Cu_3O_7$$

2. $MgAl_2O_4$ is used as white ceramic pigment and can be prepared by sol gel method as the following:

$$Mg(NO_3)_2 + Al(NO_3)_3 \xrightarrow{NaOH} \text{sol} \xrightarrow{60^oC} \text{Gel} \xrightarrow{120^oC} \text{dry materials} \xrightarrow{800^oC} MgAl_2O_4$$

3. Li_4SiO_4 prepared using ceramic method from oxides at 800-900°C and using as conductor material

$$Li2CO3 + SiO2 \xrightarrow{800^oC/24\ h} Li_4SiO_4 + 2CO_2$$

C. Calculate the wavelength (nm) in electron microscopy with voltage equal to 120 kV. ($h=6.63\times10^{-34}$ J.s, $e= 1.6\times10^{-19}$ C, $m_e= 9.1\times10^{-31}$ kg, $C= 3\times10^{8}$ m/s)

$$\lambda = h/(2mev)^{1/2}$$

$$= 6.63\times10^{-34}\ \text{J.s} / (2 \times 9.1\times10^{-31}\ \text{kg} \times 1.6\times10^{-19}\ \text{C} \times 120\,000\ \text{V})^{1/2}$$

$$\mathbf{J} = \frac{\mathbf{kg \cdot m^2}}{\mathbf{s^2}} = \mathbf{N \cdot m} = \mathbf{Pa \cdot m^3} = \mathbf{W \cdot s} = \mathbf{C \cdot V}$$

$$\lambda = 0.00355\ \text{nm}$$

D. 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 -0- 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

$$NaAl(OH)_4 + Na_2SiO_3 + NaOH$$

$$\Big\downarrow \; 25^{o}C$$

$$\text{Gel}$$

$$\Big\downarrow \; 25\text{-}175^{o}C\text{, hydrothermal}$$

$$Na_nAl_xSi_yO_z \text{ zeolite}$$

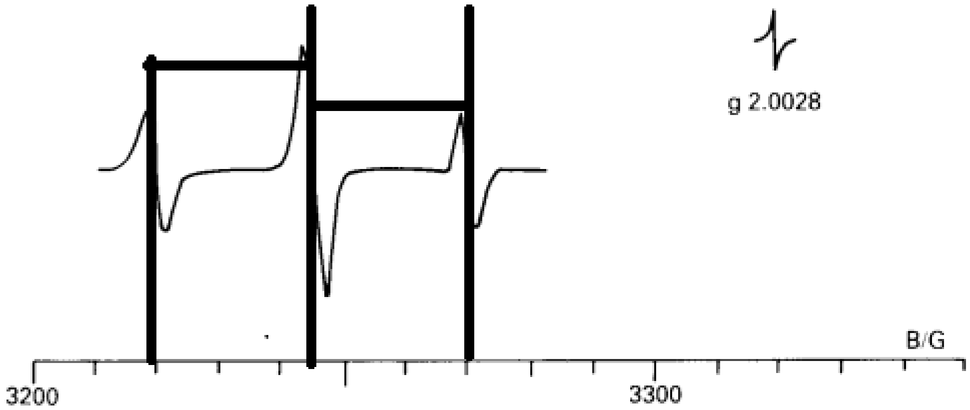
Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), and as traps for molecules so they can be analyzed. Zeolites are also widely used as catalysts and sorbents. Their well-defined pore structure and adjustable acidity make them highly active in a large variety of reactions. Zeolites have the potential of providing precise and specific separation of gases including the removal of H2O, CO2 and SO2 from low-grade natural gas streams. Other separations include noble gases, N2, O2, freon and formaldehyde. On-board oxygen generating systems (OBOGS) and Oxygen concentrators use zeolites in conjunction with pressure swing adsorption to remove nitrogen from compressed air in order to supply oxygen for aircrews at high altitudes, as well as home and portable oxygen supplies.

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

The morphology of material in cylanide and tube shape with particle size equal to 50-60 nm

4. A.



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

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

1. g(1) = 2.07122

1. g(2) = 2.05526

2. g(3) = 2.03955

a= 25 G

n. of lines = 2nI+1 =3= 2 x 3x I+1

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

$E= g\mu B= 3220 \times 2.07122 \times 9.723\text{x}10^{-12}$ J/G = $6..485 \times 10^{-8}$ J

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

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