



Benha university
Faculty of science
Chemistry department

3rd year students
Inorganic pigment chemistry
(Applied chemistry)

Date :29.12.2018
Time: 2 hours
Code: Ch324

Answer the questions only: (80 Marks)

Qu.1: (20 Marks)

- A. (10 Marks) Discuss the theory of the color analysis and explain the schematic diagram of diffuse reflectance spectroscopy.
- B. (10 Marks) Explain Pauling's rules for explanation the crystal structures of ionic compounds.

Qu.2: (20 Marks)

- A. (10 Marks) Define inorganic pigments, their properties and applications in industry.
- B. (10 Marks) Explain the classification of inorganic pigment with examples.

Qu.3: (20 Marks)

- A. (20 Marks) Write short notes on the following with example:
1. (10 Marks) sol gel method
 2. (10 Marks) Hydrothermal method

Qu.4: (20 Marks) Discuss the following with example:

1. (10 Marks) Spinel structure
2. (10 Marks) Perovskite structure

With Best Wishes,

Prof Dr. Ibrahim El-Sayed and Dr. Ayman Abdel Razik

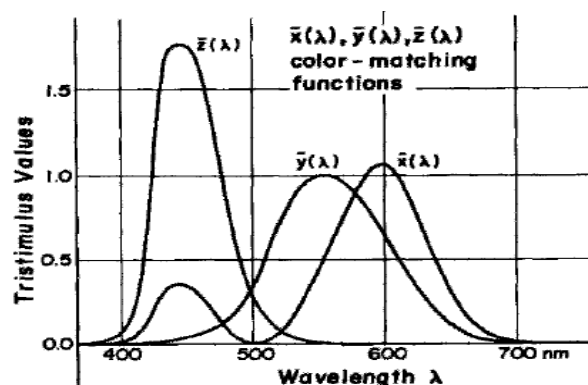
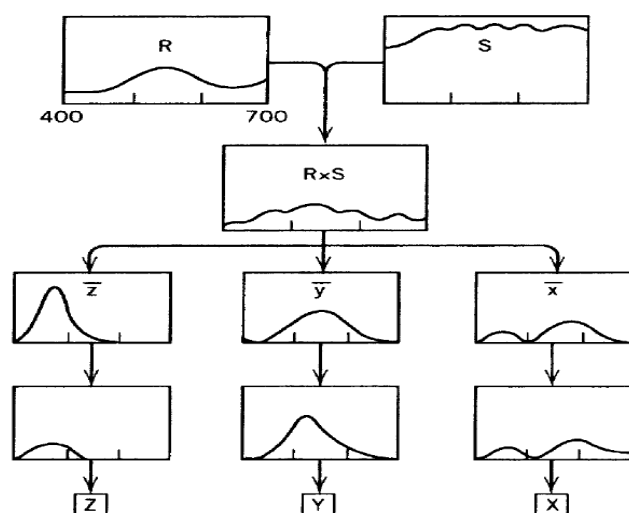
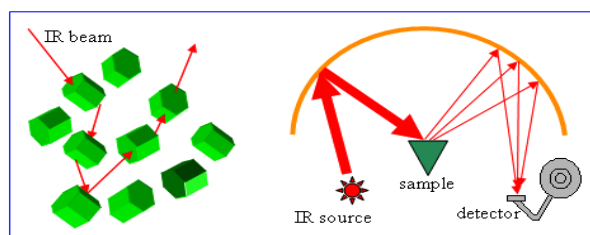
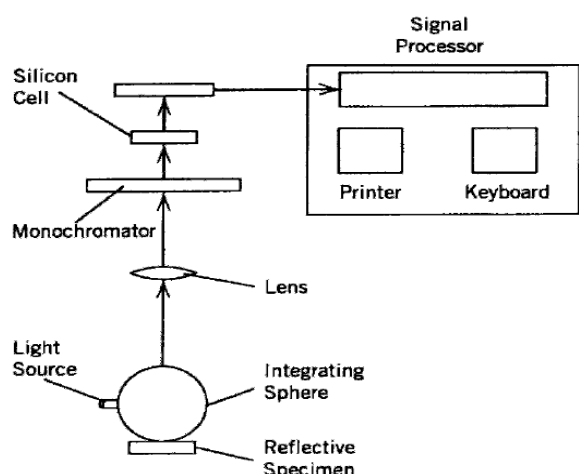
Qu.1:

- 1. (10 Marks)** Discuss the theory of the color analysis and explain the schematic diagram of diffuse reflectance spectroscopy.

Spectroscopy is the study of light as a function of wavelength that has been emitted, reflected or scattered from a solid, liquid, or gas. Absorption and Scattering: As photons enter a mineral, some are reflected from grain surfaces, some pass through the grain, and some are absorbed. Those photons that are reflected from grain surfaces or refracted through a particle are said to be scattered. Scattered photons may encounter another grain or be scattered away from the surface so they may be detected and measured. Photons may also originate from a surface, a process called emission. All natural surfaces emit photons when they are above absolute zero. Emitted photons are subject to the same physical laws of reflection, refraction, and absorption to which incident photons are bound.

Photons are absorbed in minerals by several processes. The variety of absorption processes and their wavelength dependence allows us to derive information about the chemistry of a mineral from its reflected or emitted light. The human eye is a crude reflectance spectrometer: we can look at a surface and see color. Our eyes and brain are processing the wavelength-dependent scattering of visible-light photons to reveal something about what we are observing, like the red color of hematite or the green color of olivine. A modern spectrometer, however, can measure finer details over a broader wavelength range and with greater precision. Thus, a spectrometer can measure absorptions due to more processes than can be seen with the eye. Today, spectrometers are in use in the laboratory, in the field, in aircraft (looking both down at the Earth, and up into space), and on satellites. Reflectance and emittance spectroscopy of natural surfaces are sensitive to specific chemical bonds in materials, whether solid, liquid or gas. Spectroscopy has the advantage of being sensitive to both crystalline and amorphous materials, unlike some diagnostic methods, like X-ray diffraction. Spectroscopy's other main advantage is that it can be used up close (e.g. in the laboratory) to far away (e.g. to look down on the Earth, or up at other planets). Spectroscopy's historical disadvantage is that it is too sensitive to small changes in the chemistry and/or structure of a material. The variations in material composition often cause the shift in the position and shape of absorption bands in the spectrum. Thus, with the vast variety of chemistry typically encountered in the real world, spectral signatures can be quite complex and sometimes unintelligible. However, that is now changing with increased knowledge of the natural variation in spectral features and the causes of the shifts. As a result, the previous disadvantage is

turning into a huge advantage, allowing us to probe ever more detail about the chemistry of our natural environment.



B. (10 Marks) Explain Pauling's rules for explanation the crystal structures of ionic compounds.

Pauling' Rules for Ionic Structures

1. The Cation-Anion distance is determined by summing ionic radii. The cation coordination environment is determined by radius ratio.
2. The bond valence sum of each ion should equal its oxidation state.
3. Crystals tend to avoid shared polyhedral edges and/or faces. This is particularly true for cations with high oxidation state & low coordination number.
4. In a crystal containing different cations those with large valence and small coord. # tend not to share anions.
5. The number of chemically different coordination environments for a given ion tends to be small.

Pauling's 1st Rule - Ionic Radii

The Cation-Anion distance is determined by sums of ionic radii. The cation coordination environment is determined by radius ratio. The most accurate set of ionic radii are those tabulated initially by R.D. Shannon and C.T. Prewitt and later updated by Shannon. There are two sets of radii. "Crystal radii", are based on the best estimate of the size from accurate X-ray crystallography studies. "Traditional ionic radii" are based on the sizes of oxide and fluoride ions as chosen by Pauling. The crystal radii of the cations are 0.14 Å larger while the crystal radii of the anions are 0.14 Å smaller. Ionic radii are most accurate for oxides and fluorides, and for smaller, highly charged (hard) cations in regular coordination environments. The sizes of softer ions are more dependent upon their surroundings, and thus are less transferable. Radii are dependent upon both the oxidation state of the ions involved and the coordination number.

Pauling's 2nd Rule – Bond Valence

The bond valence sum of each ion should equal its oxidation state. This idea is well known in organic chemistry where each bond has a valence of 1. So that C always has a valence sum of 4 (4 bonds), O always forms 2 bonds, H forms 1 bond, etc. Pauling took this concept and extended it to inorganic compounds, including extended ionic lattices. Pauling's proposed that the valence of a bond, s_{ij} , could be non-integer, and the sum of the bond valences around each atom, should equal its oxidation state.

$$V_i = \sum s_{ij}$$

- V_i = The oxidation state of atom i
- s_{ij} = The valence of the bond between atoms i and j .

If there are n equivalent bonds around a central atom with valence m , then valence of each bond is equal to:

$$s_{ij} = m/n.$$

Pauling's 3rd Rule

The presence of shared edges and particularly shared faces decreases the stability of a structure. This is particularly true for cations with large valences and small coordination number. When polyhedra share a common edge or face it brings the cations closer together, thereby increasing electrostatic repulsions.

Pauling's 4th Rule

In a crystal containing different cations those with large valence and small coordination number tend not to share polyhedron elements with each other. The logic behind this rule comes in part from the bonding preferences

of the anion. Consider the following example. CaWO_4 has the scheelite structure where the W^{+6} ions are tetrahedrally coordinated. The valence of the W-O bond is:

$$V_i = \sum s_{ij} v_j = 4(s_{\text{W-O}}) s_{\text{W-O}} = 1.5$$

If you were to propose a structure where two WO_4 tetrahedra shared a corner the shared oxygen would be bound to 2 W^{+6} ions. Its valence is:

$$V_{\text{O}} = 2 s_{\text{W-O}} \quad V_{\text{O}} = 2(1.5) = 3$$

This is clearly too high and a violation of the second rule. This effect is exacerbated as the cation valence increases its coordination number decreases, because s_{ij} increases.

Pauling's 5th Rule

The number of chemically different coordination environments for a given ion in a crystal tends to be small. (Rule of Parsimony) We have already discussed how ionic forces favor high symmetry and regular coordination environments

Qu.2: (20 Marks)

A. (10 Marks) Define inorganic pigments, their properties and applications in industry.

Ceramic pigments are substances that develop color in inorganic solids (ceramic or glass) and are capable of dispersing themselves at high processing temperatures without dissolution or chemical reaction. Pigments can provide a full range of colors and are often the preferred coloring agent of end users because of their high thermal stability. Pigments are used in a variety of applications, including as coatings for ceramic and glass, and in plastics and inks. The decorating industry uses pigments combined with suitable fluxes in on- and under-glaze applications.

Inorganic pigments find important in industry due to their applications in color of plastics, polymers, paints, glasses, ceramics tableware, sanitary ware, tiles and surface decoration of different classes of pottery, have traditionally been based on transition metal compounds or heavy metals. Transition metal ions or rare earth ions doped oxide pigments form a group of ceramic pigments. Ceramic pigments are inorganic products of metal oxides or compounds capable of forming metal oxides. Ceramic pigments are white or colored crystalline materials. The oxidation

state, coordination of dopants, the synthesis route, doping metals (chromophorous ions) and matrix decide the nature of color of ceramic pigments that attributed to partly filled d or f block elements. The synthesis route affects particle size distribution, and resistance to acids, alkalis. The final color of each pigment is due to the addition of a chromophore ion (usually transition metals) into an inert matrix. The host can be a single oxide (e.g. SnO₂, TiO₂) or a mixed oxide (e.g. ZrSiO₄, MgAl₂O₄). Typical examples of the chromophores are transition metal ions (Fe, Cr, Mn, Ni, Co, Cu, V, etc.) and rare earth elements (Ce, Pr, Nd). The normal spinel structure R¹O.R²₂O₃, is formed by association of a trivalent oxide (acid character) R² that present on octahedral sites and with a bivalent oxide (alkaline character) R¹ that present on tetrahedral sites. In inverse spinels, the R¹ ions and half the R² ions are on octahedral sites; the other half of the R² are on tetrahedral sites, R²(R¹R²)O₄. The mixture of these substances that has been obtained by reactions in solutions or solid-state reactions or even by milling undergoes a proper thermal treatment. They must show high thermal, chemical stability and chemical resistance at high temperatures and must be inert to the chemical action of the molten glaze with their low toxicity.

B. (10 Marks) Explain the classification of inorganic pigment with examples.

C. Q3B

D. The classification of ceramic pigment:

Tab. 1.1: Classification of inorganic pigments	
White pigments	the optical effect is caused by nonselective light scattering (examples: titanium dioxide and zinc sulfide pigments, lithopone, zinc white)
Colored pigments	the optical effect is caused by selective light absorption and also to a large extent by selective light scattering (examples: iron oxide red and yellow, cadmium pigments, ultramarine pigments, chrome yellow, cobalt blue)
Black pigments	the optical effect is caused by nonselective light absorption (examples: carbon black pigment, iron oxide black)
Effect pigments Metal effect pigments	the optical effect is caused by regular reflection or interference regular reflection takes place on mainly flat and parallel metallic pigment particles (example: aluminum flakes)
Pearl luster pigments	regular reflection takes place on highly refractive parallel pigment platelets (example: titanium dioxide on mica)

Interference pigments	the optical effect of colored luster pigments is caused wholly or mainly by the phenomenon of interference (example: iron oxide on mica)
Luminescent pigments	the optical effect is caused by the capacity to absorb radiation and to emit it as light of a longer wavelength
Fluorescent pigments	the light of longer wavelength is emitted after excitation without a delay (example: silver-doped zinc sulfide)
Phosphorescent pigments	the light of longer wavelength is emitted within several hours after excitation (example: copper-doped zinc sulfide)

The first type of pigment (idiochromatic pigment) are those in which transition metal ions are an essential part of structure and contribute to the nature of the ligand field, for example such as Cr_2O_3 (green color), CoAl_2O_4 (blue color) and other. The second type pigment (allochromatic pigment) has external effect for appearance color and this type can be sub-divided into two types: In substitution pigment, the transition or lanthanide metal ions are present in the ligand field of the host lattice and for example, the pink color of $\text{Cr}^{3+}/\text{Al}_2\text{O}_3$ as result of the present trace amount of chromium in the octahedral sites of lattice. In inclusion pigment are in which colored oxides are present in inert hosts and can be considered as solid solution type emulsion, for example $\text{Fe}^{3+}:\text{ZrSiO}_4$ red pigment as result to the entrapment of Fe^{3+} ion within zircon crystal. Inorganic pigments can be classified from various points of view.

1. Sol-gel process

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

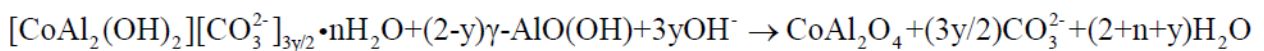
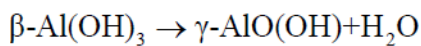
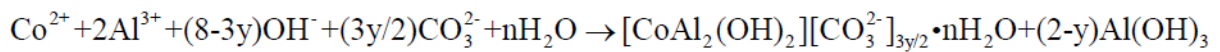
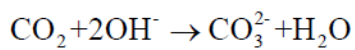
considerations. In sol-gel preparation, a solution of the appropriate precursors (metal salts or metal organic compounds) is formed first, followed by conversion into homogeneous oxide networks (gel) after hydrolysis and condensation. Drying and subsequent calcination of the gel yields an oxide product. 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.

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 $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2] \cdot [\text{A}^{m-}]_{x/m} \cdot n\text{H}_2\text{O}$. A series of chemical reactions are expressed as following:



In the case of 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 ZnAl_2O_4 , we could start with ZnCl_2 and AlCl_3 , in NaOH solution while $\text{Ba}(\text{OH})_2$ and $\alpha\text{-FeOOH}$ are used to prepare $\text{BaFe}_{12}\text{O}_{19}$.

3. This is essentially a normal precipitation method but taking place in the confinement of small aqueous solution bubbles dispersed in an oil medium. This method provides the particular advantage of avoiding agglomeration of the particles formed in the individual bubbles. This, in turn, makes possible subsequent processing routes at unusually low temperatures. To take full advantage of the method for multi-component oxides, precipitation routes need to be designed so that an intimate mixture of atoms is formed during precipitation and chemical homogeneity is maintained during subsequent processing. This offers special challenges since emulsion co-precipitations tend to be carried out with simple precursors that do not affect emulsion stability but generally show a tendency to precipitate at different rates, leading to at least partial phase segregation. A solution to this problem is presented in, for modified emulsion precipitation of BaTiO_3 . This method involves the preparation of thermally stable emulsion systems prepared by adding appropriate amounts of surfactants to a water oil system (*w/o*). Within the emulsion system, there are a small number of atoms per droplet. It is necessary that exchange of reactive species takes place between droplets in order to form a stable precipitate (nucleus). From the Einstein-Smoluchowski equation, the normal rate of the particle growth is faster than the equivalent rate of exchange between droplets. Therefore, the nucleation and growth in emulsions are retarded in comparison to those in homogeneous solution, avoiding the formation of large particles. Multi-surfactants are effective in forming a thermally stable emulsion and controlling droplet size. Other additives play a role as steric particle stabilizer after removal of water. Before the particle dispersion can be used, excess organic additives such as surfactants must be removed from the dispersion by filtration or decantation of the organic phase.

Q5:

Rutile is a mineral composed primarily of titanium dioxide, TiO_2 . Rutile is the most common natural form of TiO_2 . Three rarer polymorphs of TiO_2 are known: Anatase (sometimes known by the name "octahedrite"), a tetragonal mineral of pseudo-octahedral habit. Brookite, an orthorhombic mineral. TiO_2 (B), a monoclinic form. Rutile has among the highest refractive indices at visible wavelengths of any known crystal, and also exhibits a particularly large birefringence and high dispersion. Owing to these properties, it is useful for the manufacture of certain optical elements, especially polarization optics, for longer visible and infrared wavelengths up to about $4.5\mu\text{m}$. Natural rutile may contain up to 10% iron and significant amounts of niobium and tantalum. Rutile derives its name from the Latin *rutilus*, red, in reference to the deep red color observed in some specimens when viewed by transmitted light.

1. Spinel Structure

- Formulae – $(\text{A}^{2+})(\text{B}^{3+})_2\text{O}_4$ or AB_2O_4 or $\text{AO} \cdot \text{B}_2\text{O}_3$
- FCC Packing of anions
- Partial occupancy of both tetrahedral and octahedral sites i.e. $1/8^{\text{th}}$ of tetrahedral and $1/2$ of the octahedral sites are occupied.
- A spinel unit-cell is made up of eight FCC cells made by oxygen ions in the configuration $2 \times 2 \times 2$, so it is a big structure consisting of 32 oxygen atoms, 8 A atoms and 16 B atoms.
- Depending on how cations occupy different interstices, spinel structure can be Normal or Inverse.

1. Normal Spinel

- Chemical formula: $(\text{A}^{2+})(\text{B}^{3+})_2\text{O}_4$
- Examples are many aluminates such as MgAl_2O_4 , FeAl_2O_4 , CoAl_2O_4 and a few ferrites such as ZnFe_2O_4 and CdFe_2O_4 .
- In this structure, all the A^{2+} ions occupy the tetrahedral sites and all the B^{3+} ions occupy the octahedral sites.
- Apply bond strength rule to verify the stoichiometry
- Cations: $-\text{A}^{2+} - \frac{2}{4};$ $\text{B}^{3+} - \frac{3}{6}$
- Oxygen valence = $(\frac{2}{4} \times 1) + (\frac{3}{6} \times 3) = 2$

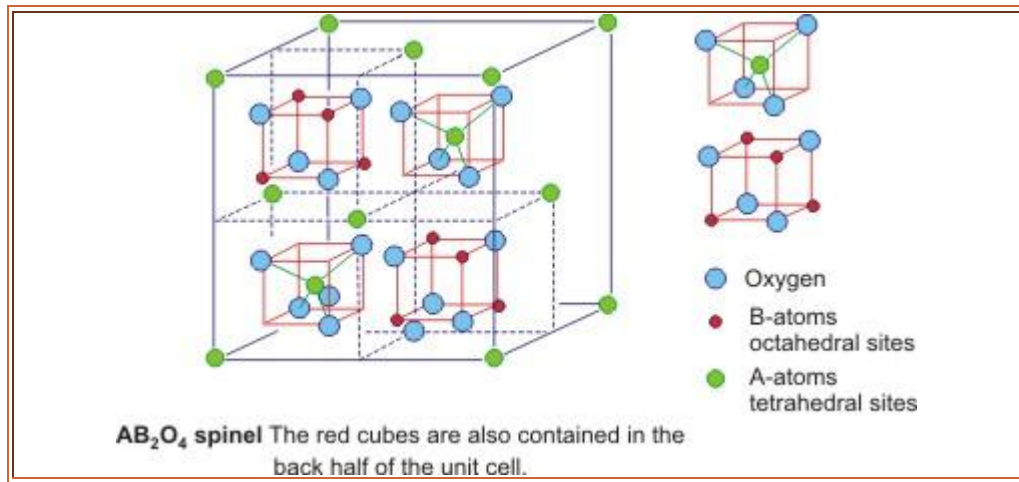


Figure 1.30 Schematic of spinel structure

Inverse Spinel B(AB)O₄

- Chemical formula: $(A^{2+})(B^{3+})_2O_4$ but can be more conveniently written as B(AB)O₄.
- Most ferrite follow this structure such as Fe₃O₄ (or FeO·Fe₂O₃), NiFe₂O₄, CoFe₂O₄ etc.
- In this structure, $\frac{1}{2}$ of the B³⁺ ions occupy the tetrahedral sites and remaining $\frac{1}{2}$ B³⁺ and all A²⁺ ions occupy the octahedral sites (now you can hopefully make sense of the formula in the previous line).