

## Chapter -2

### Ternary oxides- Ferrites, Vanadates, Tungstates and Phosphates

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#### 2.1. Introduction

Ternary oxides constitute the most fascinating class of materials exhibiting a variety of structures and properties. They play relevant role in many areas of modern technology. The electronic and magnetic properties exhibited by these oxides are noteworthy. There are oxides with metallic properties and oxides with highly insulating behaviour. There are also oxides that traverse both these regimes. The magnetic properties of perovskite ferrites are also interesting. The occurrence of recurring intergrowth structures in tungstates continues to fascinate chemists and crystallographers alike. Metal-oxide nanoparticles have unusual optical, electronic and magnetic properties, which often differ from the bulk. Preparation and processing of fine magnetic particles has been the subject of extensive research. The ferromagnetism in solids is due to the strong coupling or mutual attraction of magnetic dipole moments on the atoms. The origin of coupling behaviour is related to the outer electronic interactions of the neighbouring ions. Although the bonding in oxides is basically ionic; there is certain amount of covalency occurring between p-orbitals of the filled  $O^{2-}$  and the unfilled d-orbitals of the transition metal cations. This results in a super exchange interaction between outer electrons, which is responsible for the coupling. This super exchange interaction is characteristic of the coupled ions that both have half filled or more than half filled d-orbital. This accounts for both antiferromagnetic and

ferrimagnetic ordering in crystals. The saturation magnetization  $M_s$  and ferromagnetic transition temperature of nanocrystalline materials are considerably reduced with respect to the bulk materials [1].

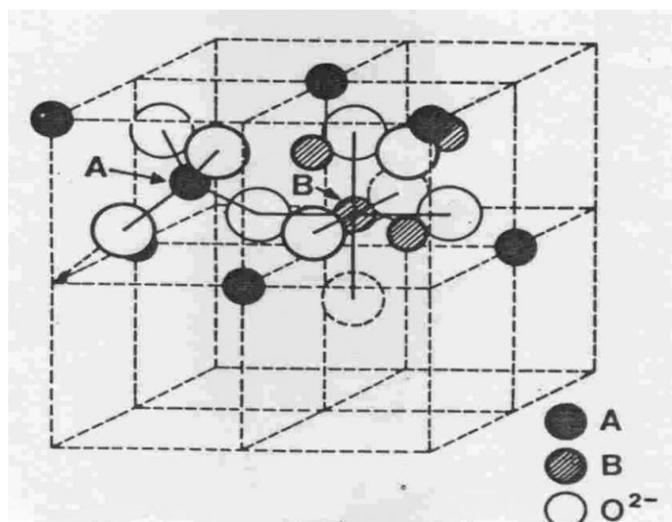
## 2.2. Ferrites

Ferrites have attracted the attention of chemists, physicists and technologists, since they exhibit magnetic as well as semi-conducting properties. The ferrimagnets are known as ferrites. The chemical formula of ferrimagnets is  $MOFe_2O_3$ , where M is a divalent ion like Ba, Sr, Zn, Cd, Mg, Ni, Co or Cu. A large family of ferrimagnets can be synthesized and used. The name of the ferrite is usually ascribed to the name of the divalent ion in the lattice [2]. Ferrites are usually non-conductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite ( $Fe_2O_3$ ) or magnetite ( $Fe_3O_4$ ) as well as oxides of other metals. Ferrites are, like most other ceramics, hard and brittle.

Ferrites have spinel structure with formula  $AB_2O_4$ , where A and B represent various metal cations, usually including iron. X-ray diffraction reveals that ferrites have a structure that may be described as a face centered cubic (f.c.c) lattice of oxygen ions closely packed together with much smaller divalent or trivalent ions placed in the interstitial sites. The basic structure of a spinel is shown in figure 2.1. The unit cell contains relatively large oxygen atoms forming f.c.c. lattice in which there are 32 octahedral sites (called B-sites) surrounded by 6 oxygen ions and 64 tetrahedral sites (called A-sites ) surrounded by 4 oxygen ions. The unit cell contains 32 oxygen ions. Out of the large number of A and B sites, only 24 interstitial sites are actually occupied by 24 cations. Of these eight are tetrahedral sites (A-sites) occupied

by divalent cations and 16 are octahedral sites (B-sites) occupied by trivalent  $\text{Fe}^{3+}$  ions. The ferrites having spinel structure of  $\text{MgAl}_2\text{O}_4$  are known as normal spinels. The spinel structure contains two cation sites for metal cation occupancy. There are eight A sites in which the metal cations are tetrahedrally coordinated by oxygen, and sixteen B sites which possess octahedral coordination. When the A sites are occupied by  $\text{M}^{2+}$  cations and the B sites are occupied by  $\text{Fe}^{3+}$  cations, the ferrite is called a normal spinel.

If the A sites are completely occupied by  $\text{Fe}^{3+}$  cations and the B sites are randomly occupied by  $\text{M}^{2+}$  and  $\text{Fe}^{3+}$  cations, the structure is referred to as an inverse spinel with the general formula  $\text{B}(\text{AB})\text{O}_4$ . In most spinels, the cation distribution possesses an intermediate degree of inversion where both sites contain a fraction of the  $\text{M}^{2+}$  and  $\text{Fe}^{3+}$  cations [3].



**Figure.2.1** Spinel Structure

Neutron diffraction studies have indicated that there is unequal distribution of  $\text{Fe}^{3+}$  ions over A and B sites. Due to this difference, there exists

a net magnetic moment per unit cell. The basic characteristics of the ferrite depend on the distribution of the  $\text{Fe}^{3+}$  and  $\text{M}^{2+}$  ions in the A and B sites. Table 2.1 gives the details of arrangements:

**Table 2. 1.** The distribution of  $\text{Fe}^{3+}$  and  $\text{Me}^{2+}$  ions in the A and B sites in Ferrites.

	A sites (8)	B sites (16)	Symbol	Examples
Normal spinel	$8\text{M}^{2+}$	$16\text{Fe}^{3+}$	$\text{M}^{2+} (\text{Fe}^{3+})_2 \text{O}_4$	$\text{ZnFe}_2\text{O}_4$ $\text{MnFe}_2\text{O}_4$ $\text{CdFe}_2\text{O}_4$
Inverse spinel	$8\text{Fe}^{3+}$	$8\text{M}^{2+}$ $8\text{Fe}^{3+}$		$\text{CoFe}_2\text{O}_4$ $\text{FeFe}_2\text{O}_4$ $\text{CuFe}_2\text{O}_4$ $\text{NiFe}_2\text{O}_4$

Spinels with cation distribution intermediate between normal and inverse are known as mixed spinels. Many of the ferrites are mixed spinels. *ie* the divalent ion may not have preference for either octahedral or tetrahedral sites. The preference is based on the internal field stabilization energy. Hence the divalent ion may be distributed among A and B sites partially [2].

The magnetic super exchange interactions between the octahedral B-sites and tetrahedral A- sites through the intervening oxygen atoms can be the reason for the two sub lattices to be antiferromagnetically ordered. Depending on the type and the preference of cations, a large number of magnetic structures are possible. There exist a very large number of ferrites and mixed

ferrites, which can be used for a number of applications. The arrangement of cations in different sites is important.

Spinel ferrites are used as thermistor materials.  $\text{NiFe}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$  have negative temperature coefficient of resistance.  $\text{BaFe}_{12}\text{O}_{19}$  and  $\text{MnFe}_2\text{O}_4$  find applications in memory devices, recording tapes, and transformer cores. Orthoferrites and hexaferrites, along with materials such as  $\text{GdCo}_5$  can support magnetic bubbles for memory applications [4].

In terms of the magnetic properties, ferrites are often classified as "soft" and "hard" which refers to their low or high coercivity of magnetism, respectively. Ferrites are widely used magnetic materials due to their high electrical resistivity, low eddy currents and dielectric loss. High frequency applications of these materials find use in the fabrication of radio frequency coils, transformer cores, and rod antennas. Their high resistivity and low hysteresis loss make them suitable to use in microwave applications and radio electronics [5,6]. Ferrites should also be mechanically strong to resist damage during machining and assembly of parts.

They find broad applications in several technological fields including catalysis, permanent magnets, magnetic fluids, magnetic drug delivery, microwave devices and high-density information storage [7, 8]. Most of these applications require particles of uniform size and shape distribution. For any particular application, the magnetic nanoparticles must possess specific properties. For example, data storage applications require particles with stable switchable magnetic states to represent bits of information, states not affected by temperature fluctuations. In bio-medical applications, the nanoparticles must exhibit superparamagnetic behavior at room temperature [9].

The properties of ferrite particles are strongly dependent on their size. Among the family of ferrite materials, cobalt ferrite, the most commercially significant particulate recording material is a well-known hard magnetic material with high coercivity and moderate magnetization and used in videotape and high-density digital recording [10]. Magnetic copper ferrites have important technological applications in various fields like magnetic information storage, biological and micro-electromagnetic devices [11].

Ferrites that are used in transformer or electromagnetic cores contain nickel, zinc, or manganese compounds, have a low coercivity and are soft ferrites. Because of their comparatively low losses at high frequencies, they are extensively used in the cores of Switched-Mode Power Supply (SMPS) and RF transformers and inductors. A common ferrite, abbreviated "MnZn," is composed of the oxides of manganese and zinc. Soft ferrites have been widely used for different kinds of magnetic devices such as inductors, transformers and magnetic heads for high frequency as their electrical resistivity is higher than those of soft magnetic alloys. Different substitutions have been incorporated to get desired electrical and magnetic properties. Knowledge of magnetic spectra of ferrites provides information whether the ferrites are useful in a given range of frequency [12-14]. Copper based ferrites have interesting electrical and magnetic properties [15, 16].

Manganese-zinc ferrites belong to the group of soft ferrite materials characterized by high magnetic permeabilities and low losses [17] and have numerous electronic applications. The Mn-Zn ferrites used in magnetic suspension should have minimum spatial and time-dependent variations in permeability [18]. Control of the electrical conductivity of Mn-Zn ferrites is

important in high frequency applications because of eddy current damping losses [19].

Permanent ferrite magnets or "hard ferrites" have a high remanence after magnetization, and are composed of iron and barium or strontium oxides. In a magnetically saturated state they conduct magnetic flux well and have a high magnetic permeability. This enables these ceramic magnets to store stronger magnetic fields than iron itself. They are the most commonly used magnets in radios [20].

Research into the synthesis and properties of nanoscale materials has exploded over the past decade due to the unique size dependent properties of nanoparticles that often differ considerably from their bulk phase materials [21, 22]. The behaviour of bulk magnetic materials is determined and influenced by the formation of domains and domain wall movement. In 1930, Frenkel and Dorfman [23] predicted that a particle of ferromagnetic material below some critical size would behave as a single magnetic domain. The critical size for single-domain behaviour depends on several factors, including particle shape and saturation magnetization. A collection of single domain particles that are not interacting with each other can reverse their magnetization only by the rigid rotation of the magnetization vector of each individual particle. As compared to the bulk material, which reverses magnetization by domain wall displacement at low fields, rigid rotation requires large reverse fields so as to overcome any anisotropies (shape, crystal, stress) that oppose the rotation. Thus, in ultra fine particles it has been possible to observe high coercivities, and this has found great application in the field of information storage [24].

Interpreting the magnetic response of bulk materials is complicated by the fact that domain wall movement can be impeded or pinned by impurities, grain boundaries, etc. in the sample. Hence a direct correlation between observed magnetic response and the quantum origins of magnetism is not readily achievable. However, if the size of the magnetic material is decreased below a critical length, domain formation is no longer energetically favoured and the particles exist as single domains [25]. Size reduction in magnetic materials resulting in the formation of single domain particles also gives rise to the phenomenon of superparamagnetism. Briefly, superparamagnetism occurs when thermal fluctuations or an applied field can easily move the magnetic moments of the nanoparticle away from the *easy axis*, the preferred crystallographic axes for the magnetic moment to point along. Upon increasing the measurement temperature, the magnetization increases and reaches a maximum at the blocking temperature,  $T_B$ , of the nanoparticle. Above the blocking temperature, the magnetization decreases and displays typical paramagnetic behaviour. The blocking temperature rises with increasing nanoparticle diameter [26]. Each particle behaves like a paramagnetic atom, but with a giant magnetic moment, as there is still a well-defined magnetic order in each nanoparticle [27]. Understanding and controlling the unique superparamagnetic properties of nanoparticles is of interest not only for fundamental research such as understanding the quantum origins of magnetism, but is crucial for practical applications such as high-density information storage, ferrofluid technology, magnetocaloric refrigeration, magnetically guided drug delivery, and magnetic resonance imaging (MRI) contrast enhancement agents [28,29]. For example, magnetic nanoparticles must be superparamagnetic at room temperatures in order to

avoid agglomeration in biomedical applications such as MRI contrast agents. However, the superparamagnetic state must be avoided in high-density information storage since superparamagnetic relaxation of the data bits will cause the magnetic moment of each bit to fluctuate and as a consequence all stored information will be lost. Spinel ferrites ( $MFe_2O_4$ ;  $M = Mg, Zn, Co, Ni$  or  $Mn$ ) are an ideal magnetic system to understand and control superparamagnetic properties at the atomic level through chemical manipulations [30]. Magnetically, spinel ferrites display ferrimagnetic ordering [31].

In most of the nanoparticle systems, the trend of decreasing  $H_c$  (coercivity) with decreasing particle size is observed [32]. Recent theoretical investigations predict that the coercivity should increase with decreasing nanoparticle size when the surface anisotropy is considered [33]. High coercivity in nanostructured cobalt ferrite thin films is also reported [34].

Nanosized ferrite materials behave as superparamagnetic materials [8, 35]. The saturation magnetization  $M_s$  and ferromagnetic transition temperature of nanocrystalline materials are considerably reduced with respect to bulk materials. Superparamagnetic materials do not show hysteresis in magnetization. In all nanoparticle systems, the saturation magnetization ( $M_s$ ) decreases with decreasing nanoparticle size. This trend is because of the increased influence of surface spin-canting (or magnetization orientation disorder at the surface) when the nanoparticle size is reduced [36]. During hysteresis measurements above room temperature, the hysteresis disappears and the nanoparticle magnetization direction follows the applied field direction.

The magnetic properties that make the ferrites useful in microwave applications arise from the interaction of the dipole moment of the electron associated with its spin with the propagating electro magnetic wave. The high values of resistivity and dielectric constant play a dominant role in making these interactions strong. The resistivity enables an electro magnetic wave to penetrate the material and the magnetic field component of the wave thus interacts with the magnetic moments of the ferrite. In some ferrites, there is a site preference of particular ions, which is strongly dependent on the temperature of preparation, the rate of cooling and heat treatment [37].

A lot of synthetic strategies for preparing nanosized magnetic ferrite materials have been reported, micelle method [38] combustion method [39-41], sol-gel method [42-44], EDTA- assisted route [45], high energy ball milling [46-48], surfactant assisted wet chemical route [49], co-precipitation method [8, 50-52] hydrothermal method [53], templated methods [54, 55], thin films by pulsed laser deposition [56], spin coating [57], electrochemical synthesis [58, 59] and flux growth [60]. While the nanoparticles obtained usually have a strong tendency to aggregate, which makes it very difficult to exploit their unique physical properties, dispersion of the nanoparticles in a matrix is one method for reducing particle agglomeration and this method allows one to stabilize the particles. In most cases, the synthesized particles are poorly crystalline and calcination at high temperature is needed to induce the high crystalline structures [53] and magnetic hardening occurs after heat treatment at a relatively high temperature [60]. The sol-gel method is a useful and attractive technique for the preparation of nanosized particles because of its advantages like good stoichiometric control and the production of ultra fine particles with a size distribution in a relatively short processing time at

lower temperatures. Poly acrylic acid (PAA) can be used as the chelating agent and it can also act like a matrix [35].

The usual ceramic method of preparing ferrispinels requires high calcinations temperature and gives inhomogeneous and aggregate particles with low surface areas. Here, in this work, we have synthesized copper ferrite and cobalt ferrite nanoparticles by sol-gel method using PAA as the chelating agent, and investigated its microwave dielectric and magnetic properties [61].

Sol-gel method is employed because of its good stoichiometric control and the production of ultra fine particles in a relatively short processing time at lower temperatures. The advantage of potentially high purity and homogeneity makes this pollution free method more attractive. In the preparation of  $\text{NiFe}_2\text{O}_4$ ,  $\text{SrFe}_{12}\text{O}_{19}$ ,  $\text{LiCoO}_2$ ,

$\text{LiMn}_2\text{O}_4$  nanoparticles, polyacrylic acid (PAA) was used as a chelating agent [35, 62-65]. The use of polyacrylic acid as a chelating agent has got the advantage of reducing the calcination temperature since the heat of combustion of PAA is utilized for the crystallization of the particles. PAA,  $(\text{CH}_2\text{CHCOOH})_x$  has more carboxylic acid groups than any other chelating agents like citric acid or polyvinyl alcohol (PVA) to form chelates with mixed cations. [35]. It also greatly aids in the formation of a cross-linked gel, which may provide more homogenous mixing of cations and less tendency for segregation during calcinations.

### 2.3. Vanadates

Nowadays vanadium oxides and their derivative compounds have attracted considerable interests due to their redox-activity and layered structures [66]. Vanadium differs from other transition elements by virtue of

its ability to adopt the trigonal bipyramidal or the square pyramidal configuration. Silver vanadium oxides are important materials, owing to their ionic properties and as a cathode material in lithium ion batteries [67].  $\text{AgVO}_3$ ,  $\text{Ag}_x\text{V}_2\text{O}_5$  and  $\text{Ag}_2\text{V}_4\text{O}_{11}$  are the most commonly occurring phases in the solid state, the detailed structural and phase analysis of which had been widely investigated [68]. The development of photo catalysts working under UV-visible region is an important theme nowadays [69]. The efficient utilization of the visible portion of the solar spectrum is essential in both solar hydrogen generation and the photocatalytic decomposition of organic pollutants. Heterogeneous semiconductors in the field of photocatalysis were investigated deeply because of its high efficiency, commercial availability and high chemical stability [70].

When the semiconductor particles are illuminated with UV or visible light, an electron promotes from the valence band to the conduction band due to photo excitation, thus leaving an electron deficiency or hole in the valence band; in this way, electron/ hole pairs are generated [71]. These electron hole pairs can either recombine or can interact separately with other molecules. Both reductive and oxidative processes can occur at/or near the surface of the photo excited semiconductor particle [72]. In aerated aqueous suspensions, oxygen adsorbed on the surface of the catalyst acts as an electron trap on the conduction band and electron/hole recombination can be effectively prevented and lifetime of holes is prolonged. A photocatalyst able to promote the decomposition of water molecules and operating in the frequency range of visible light is a primary target in solar energy storage technology.

$\text{TiO}_2$ -based photocatalysts have been the most extensively studied; however, despite great efforts, the range of frequencies in which they work is

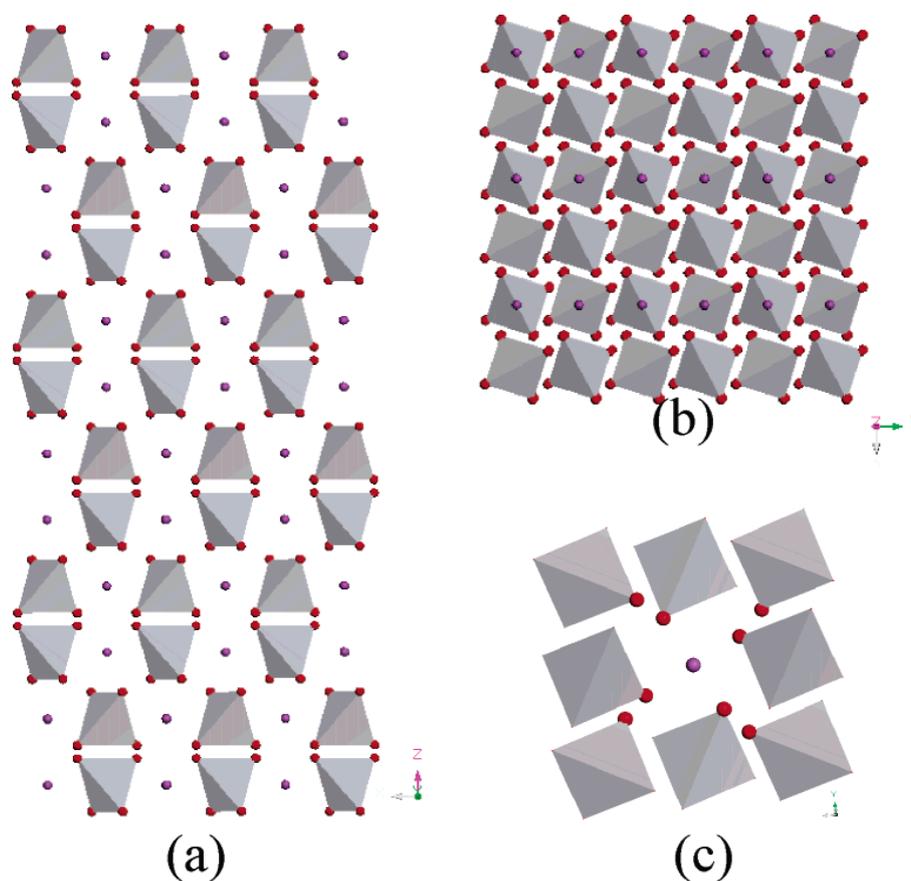
mostly limited to the ultra violet (UV) region [73]. Given this situation, photocatalytic properties of quite a few metal oxides different from  $\text{TiO}_2$  have been explored in order to try to overcome this difficulty. As a result, it was found that some vanadates show good photocatalytic activities in visible range [74, 75].

The diffuse reflection spectral analysis shows that silver vanadate has a low band gap of about 2.4 eV and is a candidate for UV-visible light driven photocatalysts [76].  $\text{AgVO}_3$  exist as three polymorphs namely  $\alpha$ ,  $\beta$  and  $\gamma$ . Silver vanadium oxide phases are mostly synthesized by solid-state reactions. Ion exchange synthesis of silver vanadates from organically templated-layered vanadates [77] and synthesis of ultra-long  $\beta$ - $\text{AgVO}_3$  nanoribbon bundles have been reported [78]. Studies on the electrical properties of silver vanadate amorphous superionic conductors and the synthesis of Ag nanoparticles supported on  $\text{AgVO}_3$  nanobelts have also been reported [79, 80]. But the soft chemistry routes rather remain unexplored for the synthesis of nanophased metal vanadates.

$\text{BiVO}_4$  has attracted attention as a ferroelastic and ion conductive material [81-86]. These properties strongly depend on the crystal form.  $\text{BiVO}_4$  has three main crystal forms, the zircon structure with tetragonal system and scheelite structure with monoclinic and tetragonal systems [83]. The phase transition occurs at 528 K between the scheelite type monoclinic  $\text{BiVO}_4$  and tetragonal  $\text{BiVO}_4$  [86-88]. Monoclinic  $\text{BiVO}_4$  shows high photo catalytic activity compared to tetragonal  $\text{BiVO}_4$  [89].

The crystal structure of monoclinic  $\text{BiVO}_4$  is shown in figure 2.2. V site in the system is surrounded by four oxygen atoms forming a  $\text{VO}_4$  tetrahedron and the typical V-O distance is 1.86-1.87 Å. Each  $\text{VO}_4$  tetrahedron

does not make contact with a subsequent  $\text{VO}_4$  tetrahedron, and the Bi site is surrounded by eight oxygen atoms located at the corners of eight different  $\text{VO}_4$  tetrahedra [90].



**Figure 2.2.** Crystal structure of monoclinic  $\text{BiVO}_4$ . (a) View from the  $[010]$  direction. O and Bi atoms are indicated in red and purple, respectively. V atoms form a tetrahedral, shown in gray, with one O atom at each vertex. (b) View from  $[001]$  direction. (c) Bi atoms are surrounded by eight oxygen atoms belonging to eight different  $\text{VO}_4$  tetrahedra.

Tetragonal  $\text{BiVO}_4$  with a 2.9 eV band gap mainly possessed an ultraviolet absorption band while monoclinic  $\text{BiVO}_4$  with a 2.4 eV band gap had a characteristic visible light absorption band in addition to the UV band. The UV bands observed in the tetragonal and monoclinic  $\text{BiVO}_4$  were assigned to the band transition from  $\text{O}_{2p}$  to  $\text{V}_{3d}$  whereas the visible light absorption was due to the transition from a valence band formed by  $\text{Bi}_{6s}$  or a hybrid orbital of  $\text{Bi}_{6s}$  and  $\text{O}_{2p}$  to a conduction band of  $\text{V}_{3d}$ . [91].

The form of  $\text{BiVO}_4$  depends on the preparation methods. Various synthesis methods for  $\text{BiVO}_4$  have been reported. Scheelite type monoclinic  $\text{BiVO}_4$  is usually obtained by the high temperature solid state reactions [82, 92] while tetragonal  $\text{BiVO}_4$  is prepared in aqueous media at low-temperatures. Monoclinic  $\text{BiVO}_4$  can also be prepared by an alkoxide method at 400 K [93]. The synthesis of crystalline  $\text{BiVO}_4$  using layered potassium vanadates is also reported [91]. Comparative studies on the photocatalytic activities of scheelite tetragonal and scheelite monoclinic  $\text{BiVO}_4$  have also been reported [86, 94].

Literature reports reveal that very few attempts have been made for the synthesis of metal vanadates under mild conditions. In this context, it would be of interest to attempt the soft chemical routes for the synthesis of vanadate nanocrystals. Here we report the soft chemical synthesis of monoclinic  $\text{AgVO}_3$  nanorods and monoclinic  $\text{BiVO}_4$  nanobars by an environmentally friendly aqueous process without using any template. The materials are synthesized under mild conditions in aqueous media. A comparative study of the photo catalytic activity of the synthesized nanophased vanadates on the degradation of methylene blue is also investigated.

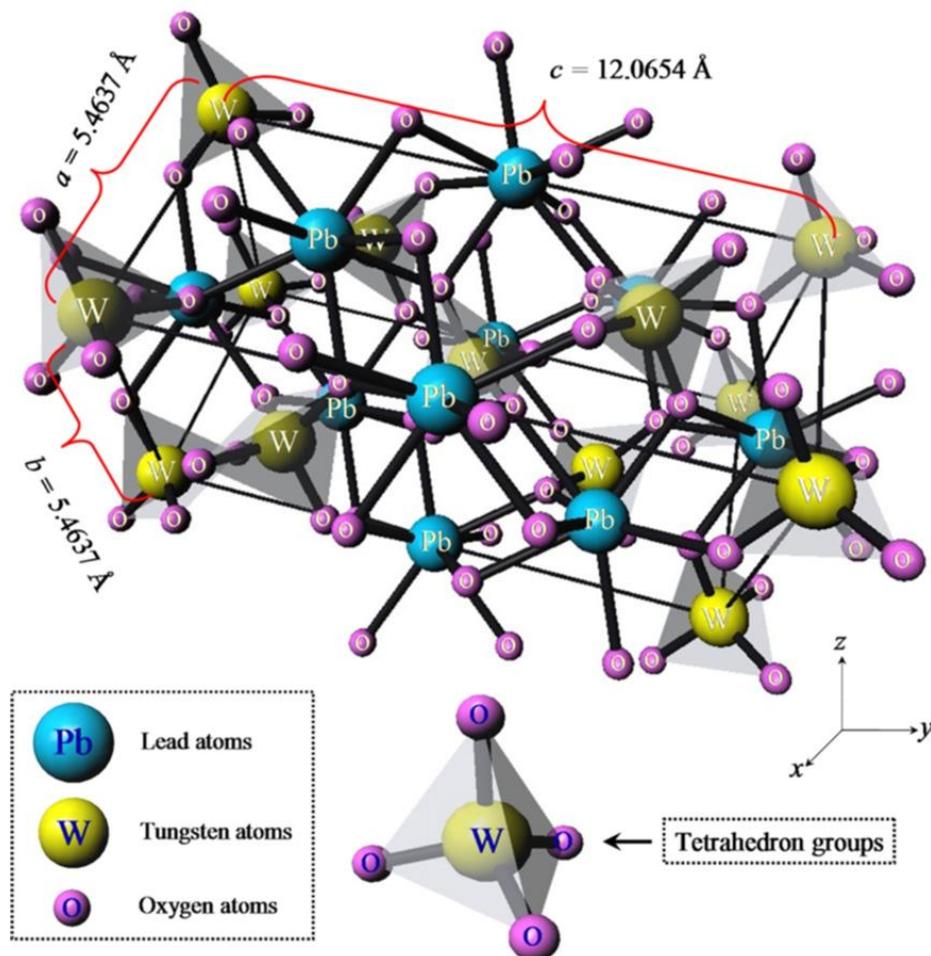
## 2.4. Tungstates

Tungstate materials have aroused much interest because of their, structural properties and potential applications in the fields of luminescence, microwave, optical, scintillating, magnetic, photocatalytic and humidity sensing [95-107]. There exist two types of structure in tungstates: wolframite and scheelite.  $ZnWO_4$  with a wolframite structure is one of the most important inorganic materials. Scheelite is a calcium tungstate mineral with the chemical formula  $CaWO_4$ . It is an important ore of tungsten. Well-formed crystals are sought by collectors and are occasionally fashioned into gemstones when suitably free of flaws. Scheelite has been synthesized *via* the Czochralski process; the material produced may be used to imitate diamond, as a scintillator, or as a solid state lasing medium [108]. In scheelite structure, the tungsten atom is in tetrahedral coordination with oxygen.

The studies on luminescence properties of nanosized phosphors are attracting current interests; because it is significant not only for applications but also for essential understanding of nanocrystals, such as confinement effect and surface effect. Studies on the luminescence center excited state absorption in tungstates have been reported [109]. Large arrays of scintillating crystals have been assembled for precision measurements of photons and electrons in high energy and nuclear physics [110]. As a self-activating phosphor, tungstate has some advantages, e.g., high chemical stability, high X-ray absorption coefficient, high light yield, and low afterglow to luminescence. Its luminescence originates due to the intrinsic structure which resulted in the charge transfer from excited 2p orbits of  $O^{2-}$  to the empty orbits of the central  $W^{6+}$  ions, and due to the structural defects.

Lead tungstate ( $\text{PbWO}_4$ ) is an important inorganic scintillating crystal, attracting many interests recently. Luminescence of  $\text{PbWO}_4$  crystals was first researched more than 40 years ago. At present, there is renewed interest in its optical spectra and scintillation properties because, since 1994, the  $\text{PbWO}_4$  crystal has been selected as the new scintillator used for the Compact Muon Solenoid (CMS) of the Large Hadron Collider (LHC) at CERN [111,112]. Single crystals of lead tungstate were chosen by the compact muon solenoid experiment in constructing a precision electromagnetic calorimeter at the Large Hadron Collider because of its high density and fast decay time [113].

Lead tungstate occurs in nature as tetragonal stolzite of scheelite type and monoclinic raspite. The optical properties of scheelite and raspite lead tungstate crystals have been reported [114]. The scheelite structure consists of isolated tetrahedra. The tetrahedra form (non touching), 1D chains. There are two directions that the "chains" line up. The raspite  $\text{PbWO}_4$  has not yet been successfully prepared in the laboratory till date. But it exists as a natural crystal, which transforms irreversibly to the scheelite around  $400^\circ\text{C}$  [115].  $\text{PbWO}_4$  with a tetragonal scheelite structure, shown in figure 2.3 is of technological importance because of its high density, short decay time, high irradiation damage resistance, interesting excitonic luminescence, thermoluminescence and stimulated Raman scattering behavior [116].



**Figure 2.3.** The tetragonal  $\text{PbWO}_4$  unit cell

This structure illustrates the tetragonal  $\text{PbWO}_4$  unit cell with space group  $I41/a$ . In tetragonal  $\text{PbWO}_4$  the tungsten atoms are coordinated to the four oxygen atoms to form a tetrahedral configuration  $[\text{WO}_4]^{2-}$ . The  $[\text{WO}_4]^{2-}$  groups present two different bonding angles between tungsten and oxygen atoms ( $107.88^\circ$  and  $112.69^\circ$ ). The  $\text{Pb}^{2+}$  cations in this unit cell are coordinated to the eight oxygen atoms forming a scalenohedra configuration [117].

Different methods for the synthesis and morphology control of  $\text{PbWO}_4$  nano and microcrystals have been reported [118-121]. Studies on yttrium doped single crystal  $\text{PbWO}_4$  [122-125], electronic structures of scheelite and scheelite-like  $\text{PbWO}_4$  [126] first-principles study on the electronic structures [127, 128], high-pressure X-ray and neutron powder diffraction studies of  $\text{PbWO}_4$  and  $\text{BaWO}_4$  scheelites [129], and studies on light yield improvement in  $\text{PbWO}_4$  crystals have also been reported [130].

Recently efforts have been devoted for the shape-controlled synthesis of  $\text{PbWO}_4$  nano and micro-crystals [131-132]. Various morphologies, including particles, rods, spheres, spindles, hollow nanospindles, dendrites, pagodas, and 18-facet polyhedrons, have been achieved by wet chemical methods [131-140]. However, most methods need a long reaction time, so it is very important to develop some other facile methods for the preparation of  $\text{PbWO}_4$  with short reaction time in mild reaction conditions.

Silver tungstate ( $\text{Ag}_2\text{WO}_4$ ) exists in three phases, namely  $\alpha$ ,  $\beta$  and  $\gamma$  phases. The phase diagram and the ionic conductivity of  $\text{Na}_2\text{WO}_4/\text{Ag}_2\text{WO}_4$  system have been reported [141]. Then kinetic and mechanistic studies of solid-state re-actions of silver tungstate with mercuric bromiodide, mercuric chlorobromide and with mercuric bromide and mercuric chloride have also been reported [142-144].

Among the tungstate crystals,  $\text{BaWO}_4$  are widely used for electro optics due its emission of blue luminescence, because of the Jahn-Teller effect on the degenerated excited state of the  $(\text{WO}_4)^{2-}$  tetrahedra [145]. It is instructive to study the synthesis and physical properties of barium tungstate which is, a potential material for designing solid-state lasers emitting radiation in a specific spectral region, and also a promising wide range Raman-active

crystal [146, 147]. Numerous efforts have been undertaken by different groups over the years for the synthesis of BaWO<sub>4</sub> nano crystals *via*, polymer micelle–assisted method [148], shape controlled synthesis using different surfactants [149], template free precipitation technique [150], polymeric cationic reverse micelles method [151], supramolecular template synthesis [152], hydrothermal synthesis [153] and by electrochemical synthesis [154].

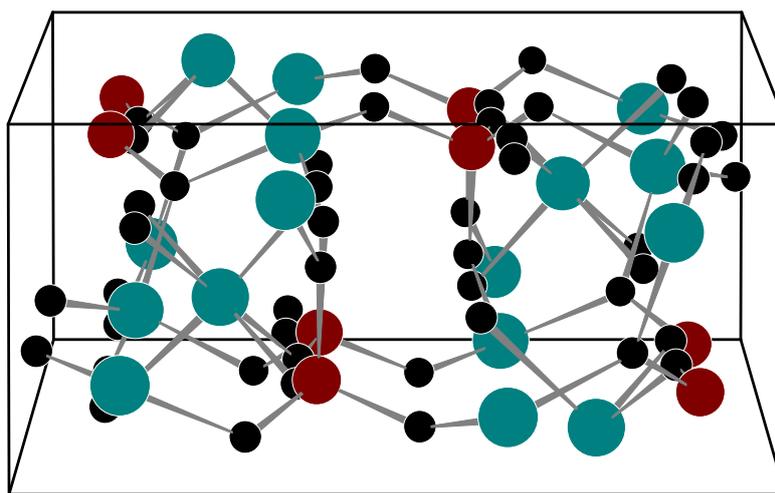
Most of these methods require high temperature and during the synthesis the WO<sub>3</sub> group has a tendency to evaporate, resulting in-homogeneous composition of tungstates. Phosphors prepared by wet chemical method have higher uniformity in particle size distribution with good crystallinity. They also exhibit high photoluminescence compared to the phosphors prepared by solid-state reaction routes [155, 156]. Moreover, in chemical precipitation, the kinetics of nucleation and growth can be adjusted by the controlled release of the anions and cations. The particle size is influenced by the reactant concentration, pH and temperature [157]. Aqueous precipitation route is simple, ecofriendly, inexpensive, highly reproducible and provides us a strategy to synthesize tungstates and other materials of similar nature.

### 2.5. Phosphates

The phosphate class is made up of minerals with a basic (AO<sub>4</sub>)<sup>3-</sup> tetrahedra where, (A represents phosphorus) The tetrahedra can be combined with metal ions on a one-to-one ratio or usually in more complex combinations with other ions like hydroxide groups (OH), uranyl groups (UO<sub>2</sub>), a halogen or even water molecules. Hydrated zinc phosphate (Hopeite) belongs to this group. Phosphate ceramics are getting attention due to their

variety of applications in optical, electrical and in prosthetics arena. They are used as fluorescent materials, dielectrics, dental cements, metal surface coatings, in fuel cells and as pigments [158-160].

Studies on transition metal phosphates are important since they are used as inorganic and biomaterials. They also find applications in catalysis, ion exchangers and as low thermal expansion ceramic materials [161]. Synthetic micro porous and layered materials are of considerable interest for a wide variety of industrial and chemical applications. When used as hosts for impurity doping, phosphates show better performance than silicates as an optical material [162]. Layered lithium zinc phosphate containing ethylene diamine is prepared by moderate temperature solution mediated conversion of a micro porous zinc phosphate [163].



**Figure 2.4.** Crystal structure diagram of zinc orthophosphate.

Orthophosphates are possibly the fastest expanding group of inorganic materials. Templated iron phosphates were discovered from the development of new solvothermal synthesis techniques [164-166]. Hydrothermal synthesis and structure refinement of open framework zinc and cobalt phosphates by the tributyl phosphate route and manganeseborophosphate were also reported [167,168]. The crystal structure of zinc orthophosphate is shown in figure 2.4.

In figure 2.4 black circles are oxygen atoms, pink circles are phosphorous atoms, and the blue circles are Zn. Also note that water basis is replaced by oxygen atoms because of the poor X-ray scattering power of hydrogen atom.

Zinc orthophosphate is a non-toxic white inorganic pigment featuring corrosion protection and adhesion capability. It is insoluble in water, soluble in acids and ammonium hydroxide. It is used in coatings for steel, aluminum, in dental cements and as phosphors. It is a flame retardant and also used as a chemically bonded ceramic material (CBC) [169]. A number of patents [170-176] are taken with regard to the zinc phosphate coatings for its use as corrosion resistant material for metal surfaces [177]. In the color televisions different phosphors are used, for their emission in the frequency ranges corresponding to each of the primary colors. Zinc phosphate doped with manganese is a well-known phosphor used in cathode tubes [178].

Cobalt orthophosphate is a violet coloured pigment called 'cobalt violet'. First developed in the early 19th century, cobalt violet was the primary permanent violet pigment available. Cobalt violets range from deep to pale shades with either a pink or blue hue. The first cobalt violets used were composed of cobalt arsenate. This highly toxic compound is now rarely used. Instead most current cobalt violets are non-toxic and are made from either

cobalt phosphate, or cobalt ammonium phosphate. Cobalt violets are used in paints [179].

To prepare metal phosphates, methods like molten salt flux synthesis [180] sol-gel synthesis [181], thermolysis/flame pyrolysis of polymer matrix based precursor solution synthesis [182], boron phosphate method [183], chemical precipitation [184,185], solid- state reaction [186], precipitation of products from bulk solutions [187,188], were developed. Moreover, most of these methods are expensive and need expensive equipments and high temperatures of synthesis and processing. To minimize these problems, soft chemical methods can be employed. But very few room temperature synthesis methods are reported till date. Here we have synthesized zinc orthophosphate and cobalt orthophosphate by an aqueous room temperature precipitation method.

### **2.6. Conclusion**

Oxides like ferrites, vanadates, tungstates and phosphates constitute the most fascinating class of materials exhibiting a variety of structures and properties. These ternary oxides in nanophase play relevant role in many areas of modern technology. Ferrites have attracted the attention of chemists, physicists and technologists since they exhibit magnetic as well as semi-conducting properties and because of their broad applications in several technological fields including catalysis, permanent magnets, magnetic fluids, magnetic drug delivery, microwave devices and high-density information storage.

Vanadium oxides and their derivative compounds have attracted considerable interest due to their redox-activity and layered structures.

Vanadates like  $\text{BiVO}_4$  and  $\text{AgVO}_3$  have low band gap energy compared to the other photocatalysts like  $\text{TiO}_2$  and are efficient visible light driven photocatalysts. Hence, they find application in the purification of wastewaters generated by the textile industries, under solar energy irradiation.

Tungstates have aroused much interest because of their luminescence behaviour, structural properties. They find potential application in various fields, such as photoluminescence, microwave, optical fibers, scintillator materials and in catalysis. As a self-activating phosphor, tungstate has certain advantages like, high chemical stability, high X-ray absorption coefficient, high light yield, and fast decay time with no afterglow.

Phosphate nanocrystals are also getting attention due to their variety of applications in optical, electrical, prosthetics and structural fields, as fluorescent materials, dielectric substances, dental cements, metal surface coatings and pigments.

The important methods for the synthesis of nanostructured oxide materials like ferrite, vanadate, tungstate and phosphates are reviewed. However, most of these methods need expensive equipments, harsh reaction conditions and are time-consuming. So it is very important to develop some other facile methods for the preparation of oxide nanomaterials using simple equipment and with a fast production rate. Currently much attention is devoted to, low cost and eco-friendly methods, thus reducing consumption of energy, space, and reagents and minimizing the generation of waste. These features are in agreement with the modern tendency towards a “Green Chemistry”. In this context, we have attempted the soft chemical routes for the synthesis of ferrite, vanadate, tungstate and phosphate nanocrystals.

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