Ferroic Materials: Synthesis and Applications

Edited by
Hardev Singh Virk

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Editor Note

Ferroics is the generic name given to the study of ferromagnets, ferroelectrics, and ferroelastics. The basis of this study is to understand the large changes in physical characteristics that occur over a very narrow temperature range. The changes in physical characteristics occur when phase transitions take place around some critical temperature value, normally denoted by Tc. Above this critical temperature, the crystal is in a nonferroic state and does not exhibit the physical characteristic of interest. In recent years, a new class of ferroic materials has been attracting increased interest. These multiferroics exhibit more than one ferroic property simultaneously in a single phase.

When I started my job as a Guest Editor with Trans Tech Publications Ltd. in 2011, I undertook publication of first volume under the title: "Ferroics and Multiferroics" which appeared in 2012. We could not cover all the envisaged topics under this Volume; hence we felt the need for the present volume: "Ferroic Materials: Synthesis and Applications". This Volume has ten Chapters, spread over areas as diverse as Magnetic Oxide Nanomaterials, Ferrites Synthesis, Hexaferrites, Spin Torque Nano-Oscillator, Ferroelectric Lattices, Flexoelectricity and Ferroelectric Materials for High Temperature Piezoelectric Applications.

Chapter 1 "Recent Advances in Synthesis, Properties and Applications of Magnetic Oxide Nanomaterials" tries to establish that oxide nanomaterials are in great demand due to their unique physical, chemical and structural properties. The nanostructured materials with desired magnetic properties are the future of power electronics. Unique magnetic properties and excellent biocompatibility of these materials found applications in pharmaceutical field also. For these applications, the synthesis of magnetic oxide nanomaterials with required properties is highly desirable. Chapter 2 deals with "Magnetic Properties of Mn-Zn Ferrites Synthesized by Microwave-Hydrothermal Process". The high values of permeability and saturation magnetization enable these materials to be the potential candidates for a number of applications, for example, in transformers, choke coils, noise filters and recording heads.

Next 2 Chapters focus on M-type and Y-type Hexaferrites, their synthesis and properties. Chapter 3 "Phase Evolution, Structural, and Magnetic Properties of Mo-Zn Doped M-type Hexaferrites" reports on the structural and magnetic properties of $BaFe_{12-4x}Mo_xZn_{3x}O_{19}$ hexaferrites with Mo-Zn substitution for Fe ions. Chapter 4 deals with "Effect of Non-ionic Surfactant" on "Microstructure, Magnetic and Dielectric Properties of Strontium-Copper Hexaferrite Powder".

The effect of surfactant concentration on phase formation, microstructure, magnetic and dielectric properties of Y-type strontium-copper hexaferrite has been investigated using XRD, SEM, TEM, VSM, dielectric and low field AC susceptibility measurement techniques.

Superparamagnetic Iron oxide nanoparticles (SPIONs) have fascinated researchers due to their vast applications in biomedical fields such as magnetic resonance imaging, cell sorting, hyperthermia, drug delivery, etc. Chapter 5 by Tokeer Ahmad and Ruby Phul describes hydrothermal synthesis, characterization and properties of SPIONs and establishes Magnetic Iron Oxide Nanoparticles as Contrast Agents. Chapter 6 presents a brief review of spin torque nano-oscillator, which has triggered extensive research interests in the field of nanomagnetism and applied spintronics in recent years. Potential applications of spin torque nano-oscillator in the fields of nanotechnology, computing, and biotechnology are highlighted by the authors.

Ferroelectric superlattices with polarization perpendicular to the surface or interface are studied within the framework of the Landau-Ginzburg theory in Chapter 7. Chapter 8 is based on "Structural, Electrical and Magnetic Properties of Ni doped Co-Zn Nanoferrites and their Application in Photo-catalytic Degradation of Methyl Orange Dye". The experimental results could be explained using Neel's collinear two-sub-lattice model and three sub-lattice non-collinear model suggested by Yafet and Kittel.

Chapter 9 "Flexoelectricity in Bulk and Nanoscale Polar and Non-polar Dielectrics" is a unique contribution for this Volume. Flexoelectricity represents the polarization due to strain gradient and has significant effects on the functional properties of nanoscale materials, epitaxial thin films, one-dimensional structure with various shape and size, liquid crystals, polymers, nano-bio-hybrid materials, etc. The authors describe the basic mechanism of flexoelectricity, brief history of discovery, theoretical modelling and experimental procedures. In Chapter 10 "Ferroelectric Materials for High Temperature Piezoelectric Applications" world-wide R & D on HT piezoelectric materials has been reviewed. There is increasing commercial and technical interest for PE actuators (ranging from electronic muscles, fuel injectors and inkjet printers to various vibrators), PE sensors (pressure and other sensors and motion detection to energy recovery), and ultrasonic imaging devices.

H.S. Virk

Editor

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Recent Advances in Synthesis, Properties and Applications of Magnetic Oxide Nanomaterials

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Keywords: Oxide Nanomaterials, Sol-gel, Coercivity, Data Storage, Bio-medicine

Abstract. Oxide nanomaterials are in great demand due to their unique physical, chemical and structural properties. The nanostructured materials with desired magnetic properties are the future of power electronics. Unique magnetic properties and excellent biocompatibility of these materials found applications in pharmaceutical field also. For these applications, the synthesis of magnetic oxide nanomaterials with required properties is highly desirable. Till now, various techniques have been evolved for the synthesis of oxide nanomaterials with full control over their shape, size, morphology and magnetic properties. In nanoscale, the magnetic properties are totally different from their bulk counterparts. In this range, each nanoparticle acts as a single magnetic domain and shows fast response to applied magnetic field. This review article discusses the synthesis techniques, properties and the applications of magnetic oxide nanomaterials. Various characterization techniques for magnetic materials have been discussed along with the literature of iron oxide, nickel oxide, and cobalt oxide nanomaterials. The challenges for further development of these materials have also been presented to broaden their rapidly emerging applications.

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1. Introduction

Oxide nanomaterials play an important role in the field of physics, chemistry and material science [1, 2]. Oxide materials exhibit insulating, semiconducting and metallic behaviour depending on their structural geometries. These materials exhibit unique physical, structural and chemical properties. In the development of advanced functional nanomaterials, the oxide nanomaterials present an essential stepping-stone. Among the oxide nanomaterials, Fe_2O_3, NiO, CoO, ZnO, TiO_2 and their nanocomposites play an important role. These materials have applications in various fields such as industrial, environmental and biological, including data storage devices, spintronic devices, photovoltaic devices, wastewater purification, sensors and catalysis, magnetic devices, etc. [3-5]. Bulk oxides are generally stable systems with well-defined crystal structures. For structural and mechanical stability, material must possess minimum surface free energy. This requirement is fulfilled in nanoscale, thus the oxide phases which are less stable in bulk materials become stable in nanomaterials [6]. Also the bulk oxides are wide band-gap materials with low reactivity. In nano-range, the band-gap of the material changes with strong influence on its chemical reactivity properties [7]. Magnetic materials are generally composed of Fe, Ni and Co metals and their oxides such as Fe_2O_3, NiO, CoO, etc. In addition to these materials, different types of magnetic materials are in research such as iron alloys (Fe–Ni, Fe–Nd–B, Fe–Ni–P, and Fe–Si) and hard and soft ferrites (Mn–Zn, Ni–Zn, Ba-ferrites) [8]. The magnetic properties of the oxide nanomaterials span from the diamagnetic, paramagnetic to the ferromagnetic and anti-ferromagnetic. Various synthesis techniques have been developed for the oxide nanomaterials such as sol-gel, co-precipitation, thermal decomposition, pulsed laser ablation, etc. [9-11]. For the study of oxide nanomaterials, their synthesis with essential requirements is a current challenge for the researchers. Various stabilizing agents such as surfactants, ligands and polymers play an important role during synthesis. In addition to stabilizing the nanomaterials, they occupy active sites at the surface of nanomaterials, thus modifying their chemical properties [12]. The next challenge is the wide knowledge of their properties: structural, optical, magnetic and electrical, and their dependence on synthesis technique used. As the size and shape of the nanomaterials depends strongly on the type of synthesis technique and chemicals used. In oxide nanomaterials, the presence of oxygen vacancies or under-coordinated atoms play an important role in their electronic structure or properties. The development of novel magnetic oxide nanomaterials is the need of hour for modern industrial growth. The two important properties shown by magnetic materials are: single domain ferromagnetism and super-para-magnetism. Magnetic nanoparticles have applications in biomedicine field (magnetic separation, hyperthermia treatments, drug delivery and magnetic resonance imaging (MRI)) when their size becomes smaller than or comparable to those of a protein, a gene, a cell or a virus. But the major problem in biological application of magnetic oxide nanomaterials is toxicity effect. To overcome this problem, a variety of coating materials are currently in study. This review article summarizes the recent advances in the field of magnetic nanomaterials and their properties and synthesis techniques. The various applications of these materials are discussed in detail.

2. Magnetic Materials

The materials which show response to the applied external magnetic field are called magnetic materials. Magnetic materials have a wide range of applications in diverse areas such as magnetic storage media, gas sensing, medical and bio-sensing applications, etc. [5-7, 13-15]. The forces generated by moving electrically charged particles in addition to their electrostatic forces contribute to the magnetic forces. In magnetic materials, the term 'magnetic dipole' is analogous to 'electric dipole'. When a magnetic material is placed in an applied field, it will experience a torque due to the alignment of its magnetic moment along the applied field. The quantity of magnetic moment determines the torque experienced by the material under external magnetic field. In an atom, each electron has a magnetic moment due to (i) the orbital motion of electrons around the nucleus, and (ii) the electron spinning around its own axis. *Magnetization (M)* represents the average magnetic field strength at any particular point due to the magnetic dipoles. *Magnetic susceptibility* (χ_m) represents the degree of magnetization for the material under external magnetic field. Mathematically, it is defined as the ratio of magnetization (M) to applied field (H); $\chi_m=M/H$. On the basis of electronic structure of materials and their response to magnetic field, the magnetic materials can be classified into five types (shown in Fig. 1):

- Diamagnetic materials
- Paramagnetic materials
- Ferromagnetic materials
- Ferrimagnetic materials
- Antiferrimagnetic materials

I. Diamagnetic materials: Diamagnetic materials have no net magnetic moment as they have no unpaired electrons in their outer shells. Diamagnetic materials have negative value of magnetic susceptibility ($\chi_m < 0$) and is temperature independent. The value of χ_m is of the order ~ (-10^{-5}) to (-10^{-6}) [16]. In an external applied field, the magnetic interactions of diamagnetic materials are weakly repulsive. Examples: copper, gold, mercury, sodium chloride, etc.

II. Paramagnetic materials: Paramagnetic materials have net value of magnetic moment due to the unpaired electrons in their outer shells. The magnetic interactions of paramagnetic materials are weakly attractive under an applied external field. The value of χ_m is small, positive and temperature dependent ($\chi_m \sim 10^{-3}$ to 10^{-5}). Examples: aluminium, sodium, chromium, etc. The paramagnetic materials obey Curie law, according to which the magnetic susceptibility is inversely proportional to temperature;

$$\chi_m = \frac{C}{T} \tag{1}$$

where C is Curie constant and T is temperature of the material. Both the diamagnetic and paramagnetic materials are considered as non-magnetic as they show magnetization only in the external applied field.

III. Ferromagnetic materials: Ferromagnetic materials show magnetization even in the absence of external magnetic field. The net magnetization in the absence of an applied field is called spontaneous magnetization. The magnetic materials exhibit ferromagnetic behaviour below the Curie temperature due to spontaneous magnetization. Whereas above the Curie temperature, material undergoes phase transition to paramagnetic state. The property of ferromagnetic materials which differentiates it from paramagnets is hysteresis loop as shown in Fig. 2.

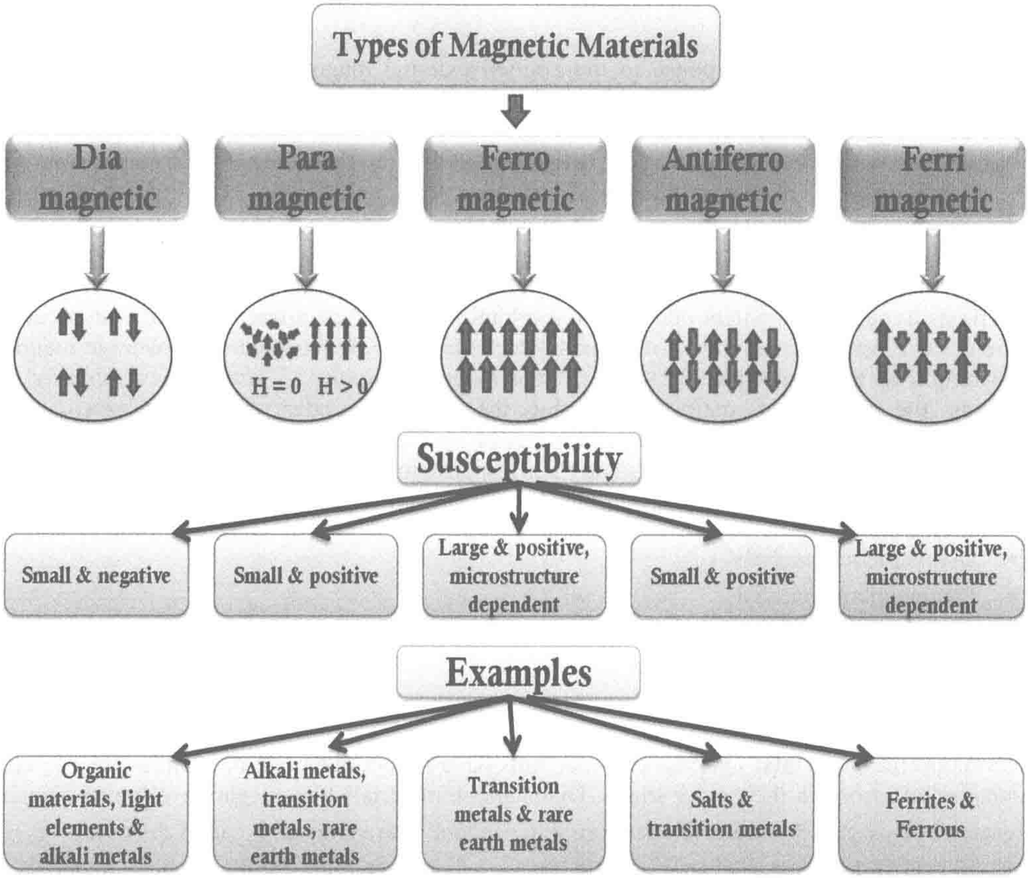

Fig. 1. Flow chart of different types of magnetic materials

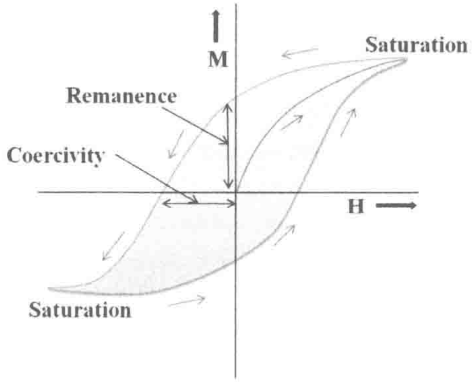

Fig. 2. Hysteresis curve for ferromagnetic materials

When a ferromagnetic material is placed in an external magnetic field, it will get magnetized in one direction and remembers that state even after the removal of applied field. The remnant magnetization when the applied field is reduced to zero is called remanence. The magnetic field in opposite direction is applied to demagnetize the ferromagnetic material. The reverse field required to drive the magnetization to zero is called coercivity. The hysteresis property of the ferromagnetic materials can be related to the existence of magnetic domains in it. Also due to this property, the ferromagnetic materials are gaining interest in magnetic memory devices. Examples: iron, nickel, cobalt, etc. These materials obey Curie-Weiss law;

$$\chi_m = \frac{C}{T-\theta} \tag{2}$$

where θ is Weiss constant.

- **Soft and hard magnetic materials:**

On the basis of hysteresis characteristics, the ferromagnetic materials can be classified as soft and hard magnetic materials.

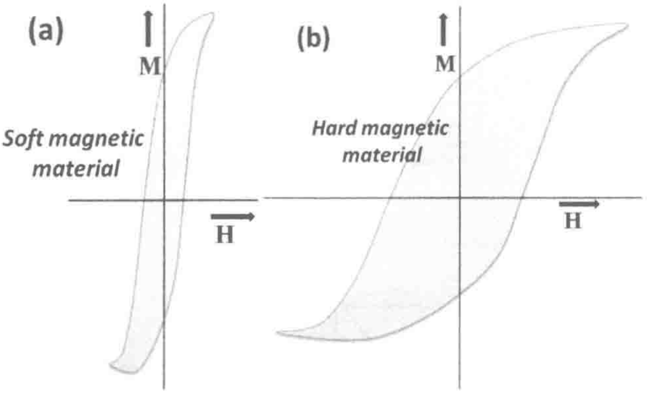

Fig. 3. Hysteresis curve for **(a)** Soft magnetic material, and **(b)** Hard magnetic material

As the area under the hysteresis loop represents the magnetic energy loss per unit volume resulting in heat generation or rise in temperature of the specimen under consideration. Soft magnetic materials are those which can be magnetized or demagnetized easily with low value of coercivity and high permeability. The characteristic hysteresis loop of soft magnetic materials is thin and narrow with small area as shown in Fig. 3(a). These materials are used in devices (motors, generators, switching circuits, etc.) which can be subjected to high alternating magnetic fields with low energy loss. Hard magnetic materials have high value of coercivity and remancence with high energy losses. The characteristics hysteresis loop for the hard magnetic materials is shown in Fig. 3(b). These materials are utilized in recording media and permanent magnets with high resistance to demagnetization.

IV. **Antiferromagnetic materials:** Antiferromagnetic materials have zero net magnetic moment as the electronic spins have antiparallel alignment to each other. The alignment of electronic spins is shown in Fig. 2. The paramagnetic materials show antiferromagnetic behaviour below Neel temperature. Examples: Cobalt oxide (CoO), nickel oxide (NiO), iron manganese (FeMn), etc.

V. **Ferrimagnetic materials:** The ferrimagnetic substances have net spontaneous magnetization due to the unequal antiparallel alignment of the magnetic moments. Ferrimagnetic materials have positive susceptibility and magnetization but weaker than the ferromagnetic materials. Examples: Iron oxides, magnetite (Fe_3O_4), yttrium iron garnet (YIG), etc.

3. Magnetic Nanomaterials

Over the past 10 years, the interest in nanotechnology has increased due to its utility in a wide range of applications. The materials with at least one dimension between 1 to 100 nm are classified as nanomaterials. The nanomaterials which show response to the applied magnetic field are called magnetic nanomaterials. As the particle size decreases, the larger number of atoms resides on the surface as compared to the core of the particle increasing the surface to volume ratio. This increased surface to volume ratio is the important factor for various structural, optical, chemical, magnetic and mechanical properties of the nanomaterials as compared to the corresponding bulk material. The magnetic properties such as magnetic moment per atom, coercivity, Curie temperature and permeability are totally different from their bulk counterparts [17].

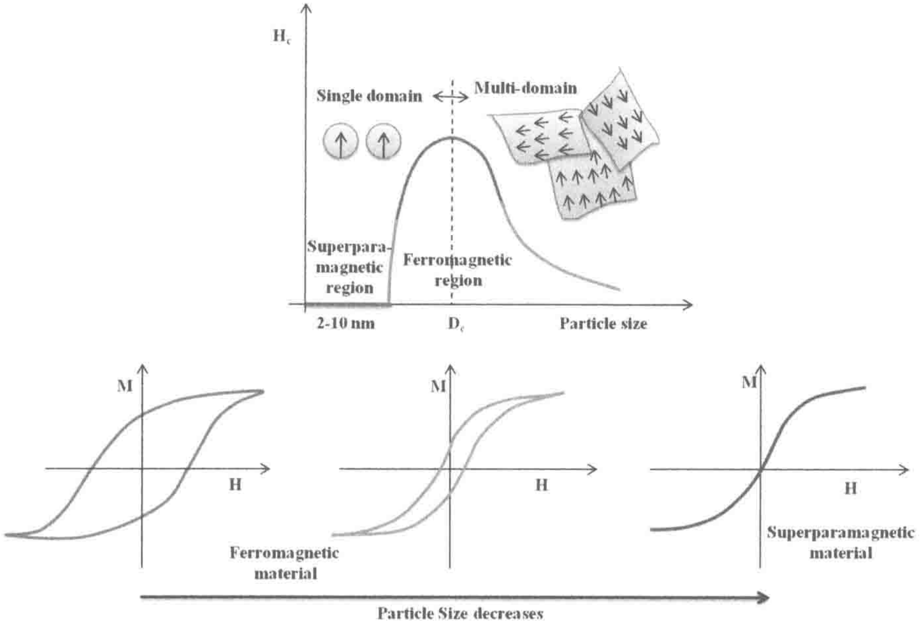

Fig. 4. Effect of decreasing particle size on the hysteresis curve of ferromagnetic material

It is well established that the magnetic materials consist of magnetic domains which resulted from a balance of magneto-crystalline anisotropy, the exchange energy and the magnetostatic energy. The magneto-crystalline anisotropy orients the magnetic moments along a particular direction, the exchange energy orients the magnetic moments in same direction and the magnetostatic energy eradicates the magnetization in the material [18]. In each domain, the magnetic moments are aligned in the same direction resulting in net magnetization in an applied field. The resultant magnetization of the magnetic material is the addition of magnetizations of different domains. When the size of the nanoparticles decreases below the critical limit, each nanoparticle behaves as a single magnetic domain and show super-para-magnetism until the temperature is above blocking temperature (T_B). Thus each nanoparticle behaves like a giant paramagnetic atom displaying fast response to the applied magnetic field. Magnetic nanoparticles (MNPs) show no hysteresis with zero or negligible remanence and coercivity as shown in Fig. 4 [19]. To analyze the magnetic properties, one has to obtain knowledge about the size, composition, shape and crystal structure of the nanomaterials plus the information about magnetization, remnant magnetization, coercivity, and blocking temperature.

In MNPs, the magnetization can be reversed through spin orientation instead of motion of domain walls. The high coercivity of MNPs is due to the spin rotation instead of domain wall motion and shape anisotropy.

In MNPs, there exist several types of defects such as dangling bonds, atomic vacancies, lattice disorder, etc. The surface atoms experience different forces or environment than the core atoms of the particle. Thus the total magnetization of the MNPs can be modelled via a core-surface or coreshell magnetic model [20]. It has been reported that the surface effects may increase or decrease the magnetization of the nanoparticles depending on the material [21, 22]. Respaud et al. [22] had reported the effect of surface defects on the magnetic properties of the CoO nanoparticles.

4. Synthesis Techniques

The major challenge in the use of magnetic oxide nanomaterials for various applications is their synthesis with controlled size and composition, desired surface properties and reproducibility. Various methods have been reported in literature for the synthesis of oxide nanomaterials and some are discussed below (shown in Fig. 5):

- Co-precipitation
- Thermal Decomposition
- Hydrothermal Method
- Sol-Gel Process
- Microemulsion
- Polyol Method
- Sonolysis
- Physical Vapour Deposition

4.1. Co-precipitation: Co-precipitation is one of the oldest and convenient methods for the synthesis of MNPs. In this process, the aqueous salt solution of metal oxides and ferrites is prepared by addition of a base (NaOH, KOH, etc.) under room temperature or at higher temperature. Usually, the oxides of iron, i.e., Fe_3O_4 and γ-Fe_2O_3 and ferrites are prepared by this method. The chemical reaction of the process can be written as:

$$M^{2+} + 2Fe^{3+} + 8OH^{-} \rightarrow MFe_2O_4 + 4H_2O \quad (3)$$

where M can be Fe^{2+}, Co^{2+}, Mn^{2+}, Mg^{2+}, Ni^{2+} and Zn^{2+}.

For the completion of the above reaction: (i) stoichiometric ratio of Fe^{3+}/M^{2+} should be 2:1, (ii) pH should be levelled between 8 and 14, i.e. basic nature, and (iii) environment must be non-oxidizing [23]. Under ambient conditions MNPs such as Fe_3O_4 are not stable and get oxidized to maghemite (γ-Fe_2O_3). As γ-Fe_2O_3 is ferromagnetic in nature, due to this reason magnetite particles are usually oxidized to convert them into maghemite [24].

Iida et al. synthesized Fe_3O_4 nanoparticles by co-precipitation process with a focus on the control of size of Fe_3O_4 nanoparticles. The size of Fe_3O_4 nanoparticles obtained by co-precipitation of ferrous and ferric ions was approximately 9 nm in diameter [23]. Sun et al. reported a simple organic-phase synthesis of magnetite nanoparticles whose size varies from 3-20 nm. They also reported that the reaction of $Fe(acac)_3$ (acac = acetylacetonate) in the presence of alcohol, oleic acid and oleylamine can be used to produce size-controlled mono dispersed Fe_3O_4 nanoparticles at high-temperature [25].

The properties of MNPs such as size, shape and composition strongly depends upon the type of salts used (e.g. chlorides, sulfates, nitrates), type of base, ionic strength of the media, the reaction temperature, the pH value, the M^{2+}/Fe^{3+} ratio and the sequence of addition, as they all play very important role in deciding the particle profile [23]. Also several reports suggested the use of performing the reaction at high temperature instead of room temperature and explained its importance in controlled crystal growth [25].

The main advantage of co-precipitation process is that MNPs can be synthesized at a large scale. Also it is the easiest method for producing Fe_3O_4 and γ-Fe_2O_3 nanoparticles [26] and has proven to be highly economical and versatile too. In this process two stages are involved [27-29]: firstly when the concentration reaches critical supersaturation, a short burst of nucleation happens and finally the slow growth of nuclei by diffusion of solutes to the surface of crystal occurs [26]. These two stages should be separated for the synthesis of mono-dispersed iron oxide. The disadvantage of this method is that the control over the particle size distribution is limited, as the growth of crystals is controlled by kinetic factors.

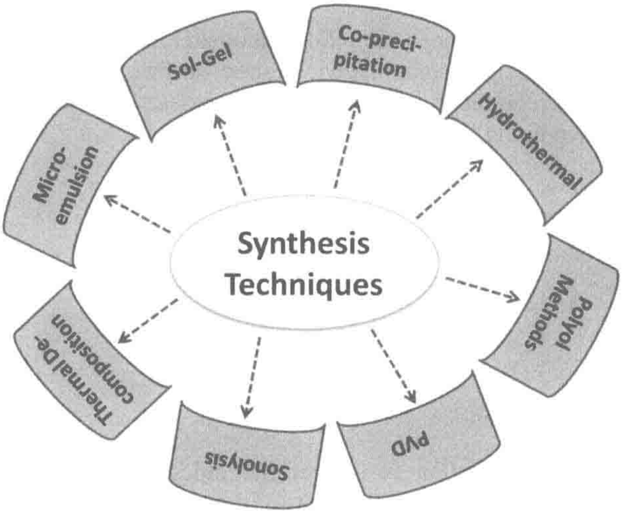

Fig. 5. Various synthesis techniques for magnetic oxide nanomaterials

4.2. Thermal Decomposition: The synthesis of high quality oxides and semiconductor nanocrystals in non-aqueous media by thermal decomposition [30, 31] has become the source of inspiration for developing similar methods for the synthesis of controlled size and shape nanoparticles of magnetic materials. High temperature decomposition of organometallic precursors can produce nanoparticles with a high level of monodispersity and also control the size of particles obtained. The precursors generally used are: $[M^{n+}(acac)_n]$, (M = Fe, Ni, Mn, Cr, Co; n = 2 or 3), carbolys (such as $Fe(CO)_5$) and $M^x(cup)_x$ (cup = N-nitrosophenyl-hydroxylamine) with organic solvents and surfactants like oleic acid and fatty acids.

Initially the formation of metal nanoparticles is done by thermal decomposition of organometallic precursors in which metal is in the zero valent in their composition such as $Fe(CO)_5$. Finally it can produce high quality monodispersed metal oxides by oxidation. However, metal oxide nanoparticles can be obtained directly by decomposition of precursors with cationic metal centers such as $Fe(acac)_3$. The deciding parameters which control the size and properties of NPs are the ratios of starting reagents which include organometallic precursors, solvents and surfactants. Other important parameters which control the size and morphology of the MNPs are reaction time and temperature [24].

Davar et al. [32] reported the novel synthesis of Ni and NiO nanoparticles with average particle size ~ 14-22 nm by thermal decomposition process using [bis(2-hydroxyacetophenato)nickel(II)] as a precursor. Yu et al. [33] reported the preparation of magnetite nanocrystals of 6-30 nm by thermal decomposition of iron carboxylate salts at 320 °C using oleic acid as oxidants. However, the nanocrystals with larger sizes ~ 20-30 nm, could be synthesized when the reaction temperature was increased to 340 °C. Hyeon et al. [34] synthesized the highly crystalline and monodispersed γ-Fe_2O_3 nanoparticles by controlled oxidation of uniform Fe nanoparticles by using trimethylamine oxide as a mild oxidant. Fe nanoparticles were generated separately by thermal decomposition of iron pentacarbonyl in the presence of oleic acid at 100 °C. The resulting particle size varies between 4-16 nm.