CHAPTER 1: General introduction

1.1 Introduction

Magnetic oxides are interesting for both basic understanding and technological applications. Generally, magnetic oxides are the compounds that contain one or more elements with oxygen and respond to magnetic field. Researchers and scientists have found different type of physical properties such as electrical, dielectric and magnetic behavior in oxide materials. Recently, they have attracted huge research interest due to a rich variety of novel properties, e.g., colossal magnetoresistance [1], half-metallicity [2], room temperature ferromagnetism [3], low temperature resistivity minimum [4], and electrically driven reversible switching [5].

1.1.1 Origin of magnetism

The magnetic moment of individual atom may originate due to,

(i) Orbital angular momentum ($\vec{L}$) due to motion of electrons around the nucleus

(ii) Spin angular momentum ($\vec{S}$) due to rotation electrons about its own axis.

Hence, total atomic magnetic moment

$$\vec{\mu}_j = -g_j \frac{e}{2m} \vec{J}, \quad \text{where} \quad \vec{J} = \vec{L} + \vec{S} \quad (1.1)$$

Most of the transition elements contribute magnetic moments due to spin alone ($\vec{S}$) and orbital momentum ($\vec{L}$) is largely quenched. Some transition elements, e.g., Co, are partially quenched and contribute large magneto crystalline anisotropy due to L-S coupling. In the case of Rare-earth elements, e.g., Ho, orbital motion is not quenched and magnetic moment is determined by total angular momentum ($\vec{J} = \vec{L} + \vec{S}$).

1.1.2 Classification of ordered magnetism

Diamagnetic materials do not posses unpaired electrons and atoms filled with electrons in shells have zero spin and zero orbital moment. Hence, there is no net magnetization in
diamagnetic materials. Orbital angular momentum is induced by an applied magnetic field and hence directed opposite to the applied field. This results in a negative magnetic moment. Superconductor is a perfect diamagnetic material.

In paramagnetic (PM) compounds, the atoms do possess permanent dipole moment due to existence of unpaired electrons. These atomic magnetic moments are randomly oriented and do not have mutual interactions in the absence of magnetic field. It is related to the tendency of a permanent moment to align along the applied magnetic field direction and magnetization changes linearly on the applied field. There are certain materials where strong interactions among the atomic dipole moments exist and the moments form domain configuration. In case of ferromagnet (FM), the spin moments are parallel inside a domain. In case of antiferromagnet (AFM), the moments are antiparallel inside the domains and the spins structure is assumed to be consisting of two sublattices, one due to up spins and second one due to down spins. Moment of each sublattice is equal, but opposite in direction, which results in zero net moment at 0 K. Above a critical temperature \( T_C \) for FM and \( T_N \) for AFM, magnetic susceptibility behave like a paramagnetic materials and can be expressed by general equation,

\[
\chi = \frac{C}{T - \theta} \tag{1.2}
\]

\( \theta = 0 \) for ideal PM, \( \theta = +T_C \) for FM, \( \theta = -T_N \) for AFM.

In ferrimagnetic materials, the magnetic domains consist of two antiparallel magnetic sublattices with unequal magnitude. As a result, each domain contributes finite magnetization, similar to that of a ferromagnet. However, temperature dependence of their paramagnetic susceptibility may be quite different.

\[
\chi(T)^{-1} = \frac{T-T_C}{C} - \frac{\xi}{T-T_N} \tag{1.3}
\]

Spinel ferrites (e.g, Fe\(_3\)O\(_4\), CoFe\(_2\)O\(_4\)) are the common example of ferrimagnetic materials.
Table. 1.1 shows some typical features of different types magnetic materials

<table>
<thead>
<tr>
<th>Type of magnetism</th>
<th>Magnetic moment</th>
<th>Susceptibility, $\chi$, examples</th>
<th>Temperature dependence of $M$ &amp; $\chi^{-1}$</th>
</tr>
</thead>
</table>
| Diamagnetism       | No dipole moment| Small, Negative Au, Cu, Zn, B Ar, N$_2$ $\sim -10^6$ to $10^5$ | ![Graph](image1)
|                    | ![Diagram](image2) |                                  |                                               |
| Paramagnetism      | Randomly oriented magnetic moments| Small, positive Pt, O$_2$, Mn, $\sim 10^5$ to $10^3$ | ![Graph](image3)
|                    | ![Diagram](image4) |                                  |                                               |
| Ferromagnetism     | Aligned parallel to each other| Large, positive Fe, Co, Ni $\sim 10^6$ | ![Graph](image5)
|                    | ![Diagram](image6) |                                  |                                               |
| Antiferromagnetism | Aligned antiparallel to each other| Small, positive Cr, CoO, MnO, NiO $\sim 10^6$ | ![Graph](image7)
|                    | ![Diagram](image8) |                                  |                                               |
| Ferrimagnetism     | Aligned antiparallel but magnitudes are not equal| Large, positive Spinel Ferrites | ![Graph](image9)
|                    | ![Diagram](image10) |                                  |                                               |
1.1.3 Disorder magnetism

1.1.3.1 Spin glass

In spin glass system spins are randomly frozen below certain temperature, known as spin freezing temperature $T_m$. Spin freezing occurs below the conventional Curie temperature of the material in ferromagnetic state [6] due to frustration between ferromagnetic and antiferromagnetic exchange interactions. There is no conventional long range order in spin glass. First characteristic of the spin glass is the appearance of peak in the real part of ac susceptibility ($\chi'$) at $T_m$, followed by the peak in the imaginary part ($\chi''$) near to the inflection point of $\chi'$ ($T$) curves. The ac susceptibility in low field is shown in Fig.1.1 [7]. Frequency ($\nu$) dependence $\chi'$ and $\chi''$ peak follow Vogel-Fulcher law [6]

$$\nu_m = \nu_0 e^{\frac{E_a}{(T_m - T_0)}}$$

(1.4)

$T_0$ measures the strength of interactions between spins entities/clusters and $T_m$ is the freezing temperature at frequency $\nu_m$.

Fig.1.1 Temperature dependent ac susceptibility, real $\chi'$ (a, c) and imaginary $\chi''$ (b, d), for La$_{1/3}$Ca$_{2/3}$MnO$_3$ nanoparticles [Ref. 8].
1.1.3.2 Superparamagnetism: a typical size effect

When particle size of a ferromagnet is reduced from µm to nm scale, coercivity (H_C) goes through a maximum and then decrease to zero, as shown in Fig. 1.2. H_C increases with decreasing particle size in multi domain (MD) state and achieving maximum at a critical size D_S. This is followed by the decrease of H_C on further decreasing the particle size in single domain (SD) state. Below the critical size D_P the H_C becomes zero and the single domain particles become superparamagnetic. The size of the ferromagnetic particles or clusters is so small that they can randomly flip in direction of local anisotropy axis, like paramagnetic atoms, under thermal fluctuations. Basic difference is that each individual atomic dipole moment in paramagnet is independently influenced by external magnetic field, where as a group of atomic magnetic moments collectively respond to magnetic field in superparamagnetic material. Below a typical measurement temperature (T_B), known as blocking temperature, the thermal energy (k_B T) of the particles is insufficient to overcome the anisotropy energy barrier (E_B=KVsin^2θ) and the magnetic domains relax along their local anisotropy axes. This results in a gradual decrease of magnetization on further decreasing temperature. The blocking phenomenon is shown in Fig. 1.3.

![Image of figure 1.2](image1.png)

**Fig.1.2 Variation of intrinsic coercivity (H_C) with particle diameter [Ref. 9].**

Generally, T_B decreases with the decrease of particle size [Fig. 1.3(a)] and magnetic irreversibility between ZFC and FC magnetization curves occurs below T_B [Fig. 1.3(b)]
Fig. 1.3 (a) Variation of $T_B$ with decreasing particle size in Co nanoparticles [Ref. 10], (b) Temperature dependence of magnetic susceptibility for zero field cooled (ZFC) and field cooled (FC) modes for CoFe$_2$O$_4$ nanoparticles at different magnetic fields [Ref. 11].

1.1.4 Interaction in magnetic oxides

1.1.4.1 Various exchange interactions in magnetic oxides

The magnetism occurs in magnetic materials by different exchange interaction, which can be explained by following exchange interactions,

(a) Direct Exchange interaction

(b) Indirect Exchange interaction

   (i) Superexchange Interaction

   (ii) Double Exchange Interaction

Direct exchange interactions dominate when electron wave functions of two neighboring atoms with directly overlap. It is strong but short-ranges order, which decreases rapidly as the ions separated. The electrons spend most of their time in between neighboring atoms when inter-atomic distance is small. According to Heisenberg spin-spin exchange interaction in solid materials can be represented by $H = -\Sigma_i\Sigma_{ij} J_{ij} S_i S_j$ \hspace{1cm} (1.5)
J<sub>ij</sub> is called exchange integrals, J<sub>ij</sub> > 0 for FM, and J<sub>ij</sub> < 0 for AFM and J<sub>ij</sub> = 0 for PM.

In most of the magnetic oxides, magnetic interactions between magnetic ions occur via non-magnetic anions. This is known as superexchange interaction, as shown in Fig 1.4. In manganite (AMnO₃) Mn⁴⁺-O²⁻-Mn⁴⁺ superexchange interaction is antiferromagnetic.

**Fig.1.4 Super exchange interaction in manganites Mn⁴⁺–O²⁻–Mn⁴⁺.**

Double exchange interaction (DE), as shown in Fig. 1.5, is another example of indirect interaction. This was proposed by Zener [12] to explain the ferromagnetism in manganites. Strong Hund’s coupling makes electron hopping most probable when the spins of neighboring (Mn³⁺, Mn⁴⁺) spins are parallel. Double exchange is always ferromagnetic, unlike antiferromagnetic superexchange interactions.

**Fig.1.5 Double Exchange Mechanism in Manganites for Mn³⁺–O²⁻–Mn⁴⁺ path.**

1.1.5 Structure of selected magnetic oxides

1.1.5.1 Spinel oxide

Most of the spinel ferrites (formula unit AB₂O₄) form cubic spinel structure with oxygen anions in fcc positions and cations in the tetrahedral (A) and octahedral (B) coordinated
interstitial lattice sites, forming the A and B sublattices [13]. The unit cell contains 32 oxygen anions and 24 cations, where 8 of the cations distributed on the 64 available A sites and 16 on the 32 available B sites. Depending on the nature (magnetic/non-magnetic) and distribution of cations among A and B sublattices, spinel oxide can exhibit the properties of paramagnet, ferrimagnet, and antiferromagnet. Spinel oxide can be classified into two groups; one is normal spinel where divalent (D$^{2+}$) ions occupy A sites whereas trivalent (T$^{3+}$) cations occupy B sites. If A sites are completely occupied by T$^{3+}$ cations and B sites are occupied by D$^{2+}$ and T$^{3+}$ cations, the structure is referred to as an inverse spinel. When both A and B sites are occupied by the mixture of D$^{2+}$ and T$^{3+}$ cations, the spinels are known as mixed spinel. For example, our studied spinel Co$_2$FeO$_4$ [14] and CoHo$_{0.05}$Fe$_{1.95}$O$_4$ [15] belong to the mixed class. There are three superexchange interaction constants $J_{AA}$ (A-O-A), $J_{BB}$ (B-O-B) and $J_{AB}$ (A-O-B) among the ions in A and B sublattices. All the super exchange interactions are antiferromagnetic in nature. The magnitude of interactions follows the order $|J_{AA}| < |J_{BB}| < |J_{AB}|$ for long-ranged ferrimagnet. $J_{AB}$ is so strong that one can assume moments in A and B sub-lattices are ferromagnetic, but two sub-lattices are antiparallel to each other.

![Fig.1.6 Schematic unit cell of crystal structure of spinel oxide.](image)

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1.1.5.2 Perovskite oxide

In ideal perovskite (formula unit $\text{ABO}_3$) A site cations are typically larger than B site cations. The A cations are surrounded by 12 oxygen anions and B cations by 6 oxygen anions. Few of the perovskite materials (e.g., $\text{CaTiO}_3$) follow ideal cubic structure, where A atoms sits at corner positions and B atoms sits at body center position and oxygen atoms sits in the face center positions. The distortion in perovskite structure is described by tilting of the $\text{BO}_6$ octahedra, which occurs due to cation size mismatch. For example, the studied manganite $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ stabilizes in rhombohedral structure.

![Fig.1.7 Ideal ABO$_3$ perovskite crystal structure.](image)

1.1.5.3 Double perovskite

In ideal double perovskite structure (formula unit $\text{A}_2\text{BB'}_2\text{O}_9$) A is divalent alkaline cation ($\text{Ca}^{2+}$, $\text{Sr}^{2+}$, $\text{Ba}^{2+}$, etc) or trivalent ($\text{La}^{3+}$, $\text{Nd}^{3+}$, etc) rare earth cation, and B and B$'$ are transition metal ions located on octahedrally coordinated interstices of the closed packed lattices having a simple cubic configuration. In these oxides, two perovskite units $\text{ABO}_3$ and $\text{AB'}_2\text{O}_3$ form alternative arrangement of rock salt (NaCl) type structure. There are two types of lattice disorder, viz., anti-site defects (ASD) and anti-phase domains (APD) in double perovskite system [16]. ASD arises due to exchange of Fe and Mo moments among B$'$ and B (wrong) sites of double perovskite structure. For example, in $\text{Sr}_2\text{FeMoO}_6$, the superexchange path –Fe-O-Mo-O-Fe-O-Mo- is replaced by –Fe-O-Fe-O-Mo-O-Mo-O after introducing ASD. APD
Fig. 1.8 Ideal crystal structure of double perovskite ($A_2BB'O_6$).

Fig. 1.9 Normal structure of $A_2FeMoO_6$ (a) and antiphase boundary (dashed line) where the localized magnetic moments exhibit an antiferromagnetic coupling in 110 plane (b). Large arrows denote magnetizations in each ferrimagnetic domain [Ref. 17].

originates between two coherent crystallites with different octahedral sites (B and B’) occupied by similar (Fe or Mo) atoms and forms the interfacing planes of Fe–O–Fe (strongly antiferromagnetic) or Mo–O–Mo (weak magnetic or paramagnetic) bonds.

1.1.6 Core-shell model for magnetic nanoparticles

R.H. Kodama et al. [18] proposed a core-shell model to explain some unusual magnetic properties, i.e., decrease of magnetization, lack of high field magnetic saturation, etc., of ferrimagnetic nanoparticles. According to this model, a magnetic nanoparticle is consisting of
two parts (as shown in Fig. 1.10 b), viz., central part (known as core) and outer part (known as shell). The core spins essentially bulk spin structure (Fig. 1.10(a)), more ordered than the shell spin structure. The shell spins disordered due to surface spin canting and frustration effects.

![Typical ferromagnetic domain in bulk material](image1.png)

**Fig. 1.10** (a) Typical ferromagnetic domain in bulk material, (b) Spin alignment in nano sized ferromagnetic domain, forming Core-Shell structure of spins.

Kodama model explained the decrease of magnetization in many ferro/ferrimagnetic nanoparticles [19], but not applicable to describe magnetic enhancement in antiferromagnetic nanoparticles. This is successfully explained by the core-shell model proposed by Bhowmik et al. [20]. According to this model, the core is essentially antiferromagnetic and the shell consists of frustrated spins. In this model the Heisenberg exchange interactions between two neighboring spins expressed as

\[ H_{\text{EX}} = \alpha J_{\text{EX}} \Sigma_{ij} S_i S_j \cos \theta_{ij} \]  

(1.6)

Here \( \theta_{ij} \) is the angle between spins i and j and \( 0^0 \leq |\theta_{ij}| \leq 180^0 \) and \( J_{\text{ex}} \) is exchange integral constant. Total magnetization of the particle will be

\[ M = \alpha M_{\text{shell}} \Sigma_{ij} \cos \theta_{ij} + (1-\alpha) M_{\text{core}} \]  

(1.7)

Here \( \alpha \) denotes the shell thickness, which increases with decreasing particle size.

**1.1.7 Electrical resistivity and magnetoresistance in magnetic oxides**

The electronic charge transport in magnetic oxides can be explained by hopping of electrons or holes to adjacent sites. Electrical conductivity \( \sigma \) is the inverse of the resistivity (\( \rho \))
such that $J = \sigma E$. The resistivity ($\rho$) can be obtained from the measurement of resistance (R) of the sample and applying Ohms law $V=IR$. Here, $I$ is the current passing through the sample and $V$ is the voltage developed across the sample. Temperature dependence of resistivity in metals follows the law: $\rho(T) \sim AT^\alpha$, whereas $\rho(T)$ of semi-conductor and insulator follows Arrhenius law:

$$\rho(T) = \rho(0) \exp(E_a/k_B T)$$

(1.8)

When electrical resistivity of magnetic materials changes with applied magnetic field ($H$), the phenomenon is known as magneto-resistance (MR) and MR is calculated by

$$MR = \left[\frac{(\rho(H)-\rho(0))}{\rho(0)}\right] \times 100 \%$$

(1.9)

$\rho(0)$ indicate the resistivity in the absence of magnetic field. The huge change of MR, known as colossal magnetoresistance (CMR) in Fig. 1.11 (a), occurs mostly in transition metal oxide, (e.g., perovskite, double perovskite). Some nano-magnetic materials have shown a sharp decrease of MR within low field regime, known as Low Field Magnetoresistance (LFMR) (Fig.1.11 b). The LFMR is related to the tunneling of spin polarized electrons across the grain boundaries [21]. On the other hand, MR changes almost linearly at higher magnetic field that is known as High Field Magnetoresistance (HFMR) [22]. The slow increase of the MR at high field is attributed to disordered spins at grain boundaries.

Fig. 1.11 MR with temperature variation (a) for La$_{0.75}$Ca$_{0.25}$MnO$_3$ [Ref. 23], and as the function of field (b) for La$_{0.7}$Sr$_{0.3}$MnO$_3$ [Ref. 24].
1.1.8 Dielectric properties in magnetic oxides

When a dielectric is placed in an electric field $E$, electric charges do not flow through as in a metallic conductor but ions are slightly displaced from their equilibrium positions. This induces electric dipoles in an internal electric field $E'$, which reduces the overall field within the dielectric itself. In linear dielectrics, induced electric moment ($p$) is directly proportional to the intensity of local electric ($E'$) field acting on the particle i.e., $p \propto E'$ or $p = \alpha E'$. The constant $\alpha$ is called molecular polarizability, which is a microscopic electrical parameter of dielectric. Since, electric polarization ($P$) is defined as the dipole moment per unit volume, we can write $P = np = n\alpha E'$, $n$ the number of molecules per unit volume.

There are four mechanisms which can contribute to the polarizability ($\alpha$).

(i) **Electronic Polarization** ($\alpha_e$) arises when electrons are displaced from their equilibrium positions with respect to the atomic nucleus. It is extremely fast with its resonant frequency ($10^{15}$ Hz) in the ultraviolet of electromagnetic spectrum.

(ii) **Atomic or Ionic Polarization** ($\alpha_a$) is found in molecules that consist of two ions with opposite charge, e.g., NaCl. It resonates in the infrared range ($10^{12}$-$10^{13}$Hz) of electromagnetic spectrum and at a frequency characteristic of the bond strength between the ions.

(iii) **Orientation or Dipole Polarization** ($\alpha_o$) occurs largely due to motion of charged ions between the interstitial positions within the ionic structure of insulator. It is observed in those dielectrics that contain permanent dipole moments. The dipoles are oriented randomly in the absence of external electric field and will be aligned along field direction. Such polarization occurs at frequency range $10^3$-$10^6$ Hz at room temperature.

(iv) **Interfacial or Space charge polarization** ($\alpha_s$) occurs at the interfaces of heterogeneous micro-structure of materials or between electrodes and solids. The charge piled up at the interfaces produces a localized polarization when frequency of ac field is sufficiently low ($< 10^3$). Space charge (or interfacial) polarization is the only type of electrical polarization that accompanied by a macroscopic charge transport.

Hence, total polarizability of a dielectric material $\alpha = \alpha_e + \alpha_a + \alpha_o + \alpha_s \quad (1.10)$
1.1.9 Recent work on magnetic oxides

Despite the interesting features of coexisting electric and magnetic properties in oxides, there is enough room to innovate new magnetic oxides [25, 26]. Nanoparticles of magnetic oxides exhibited interesting electric, magnetic and dielectric properties compared to its bulk counterpart. Sivakumar et al. [27] reported an enhancement of dielectric constant in nanosized CoFe$_2$O$_4$ particles. The same group observed [28] that dielectric loss in nanocrystalline Mn-Zn ferrite is nearly one order less than the magnitude of bulk Mn-Zn ferrite. George et al. [29] found high permittivity and conductivity in CoFe$_2$O$_4$ nanoparticles. Markovich et al. [30] observed the suppression of antiferromagnetic order in La$_{1/3}$Ca$_{2/3}$MnO$_3$ nanoparticles. The low temperature resistivity minimum in perovskite and double perovskite is still a matter of debate. Chen [31] et al. attributed the low temperature resistivity minimum in La$_{2/3}$Ca$_{1/3}$MnO$_3$ to the competition between quantum Kondo effect and three dimension electron-electron interactions. However, Rozenberg [32] and others [33] argued low temperature resistivity minimum as a simple grain boundary effect. Double perovskite structured A$_2$FeMoO$_6$ (A=Sr, Ca) exhibited interesting properties, such as CMR, LFMR and HFMR. Gupta et al. [34] found a remarkable increase in MR (≈ 73 %) on polyaniline-La$_{0.67}$Sr$_{0.33}$MnO$_3$ composite.

1.1.10 Applications of magnetic oxides

Spinel ferrites are technologically important due to high electrical resistivity, dielectric constant and low dielectric loss. Ferrites are extensively used in electronic applications such as transformers, filters and recording media [35, 36]. They are useful as catalyst and humidity sensors [37]. Ferrite nanoparticles are used in magnetic resonance imaging, targeted drug delivery, catalysis, biomedicine, high-density data storage and water treatment [38-40]. Some perovskite (La$_{1-x}$A$_x$MnO$_3$, A=Sr, Ba, Ca etc.) and double perovskite (A$_2$FeMoO$_6$, A=Sr, Ba, Ca etc.) materials exhibit ferromagnetic-metallic behavior at room temperature. These materials are promising candidates for spintronics and other technological applications [41]. GMR read head, one of the spintronics devices, detects the stored data by a change of resistance in magnetic field of the bit. Perovskite materials have special attraction for their possible applications in heterogeneous catalysis [42, 43]. Sr$_2$FeMoO$_6$ can used as a promising anode material for LaGaO$_3$-based solid oxide fuel operating with both H$_2$ and dry CH$_4$ [44].
1.1.11 Aim of this thesis work

- This work was designed to study the magnetic, electric and dielectric properties of different magnetic oxides with different crystal structures, e.g., ferrites (cubic spinel structure), manganites (rhombohedral structure) and double perovskite (monoclinic and tetragonal structure) and outline the connectivity between crystal structure, grain size, magnetic core-shell structure and physical properties in nanocrystalline and bulk magnetic oxides.

- This thesis work would like to study the physical properties of some magnetic oxides, where the magnetic exchange interactions are indirect type, either super exchange class (ferrites, double perovskite) or double exchange class (manganite).

- Second focus is to synthesize the materials using the novel techniques of mechanical alloying/milling with subsequent annealing at different temperature, and compare their properties with the reported work of similar compound prepared by chemical routes. Depending on the nature of material and interest, some of the studied oxides will be synthesized using chemical and solid state sintering routes.

References