Chapter 1

Introduction and Literature Review

1.1. General introduction:

Today, when the global life is prevailing on the roof of technology dominated by tuned electronic devices, there is an incredible search for new materials having multifunctional applications. Nanoparticles possessing fascinating electronic, optical, ferroelectric and magnetic properties based on their chemical composition, dimension and growth route are becoming increasingly popular for such multifunctional applications. One dimensional structure of nanoparticles draws attention of research community for the nanoengineering of surfaces and the building of functional nanostructures that are advantageous in chemical and biosensors, optoelectronics, drug delivery, photocatalysis, etc. The term “nanotechnology”, first used by Taniguchi in 1974 [1, 2], encompasses growth technique and property of materials with a large scale of 1-100 nm in at least one dimension. The famous phrase of Richard Feynman in the year 1959, “There’s Plenty of Room at the Bottom” [3] delineate many notable potential concepts for exploitation at the atomic and nanoscale. Nanotechnology encompasses a prospective collection of technologies in the area of science and engineering for electronics, spintronics, power generation, disease detection and treatment, etc. The substantial progress in nanomaterials research took place in the last twenty five years, driven by immense advances in researchers’ skill to manipulate matter in atomic level and the recognition of the unique, size dependent properties of nanomaterials [2, 4]. The potential and unique characteristics of nanoscale materials give a great impetus for the manufacture of new generation high quality nanodevices [5, 6].

Among various nanoscale materials, wide band gap II-VI binary compounds such as ZnO, ZnS, ZnSe, ZnTe, CdS, CdTe etc. are important for optoelectronic devices and light-emitting devices in the lower wavelength region of visible light. Most of these materials are characterized with a direct band gap having high optical absorption and emission coefficients. Such II-VI semiconductors are potential candidates for application in transparent electrodes, catalysis, solar cells, electroluminescent devices and other relevant technological devices. In fact these metal oxide nanoparticles having tunable optical, electrical and magnetic properties [7, 8] have drawn considerable research attention. While in bulk form these metal oxides have found utility in industrial catalytic developments and electronic submissions; on the nanoscale, those have promising applications in lasers, gas sensing, organic pollutant degradation and magnetic storage etc.

Among the II-VI compounds, ZnO is explicitly superior to other compounds because of its chemical stability, high thermal conductivity and high prospect of tuning various optical, electrical and magnetic properties and has been widely investigated. In bulk it is characterized as a direct wide band gap (3.37 eV) semiconductor [9]. The wide band gap of the ZnO composites makes it promotable in the area of high power and high temperature operations with low electronic noise. ZnO is an *n*-type, multifunctional semiconductor under ambient environments [10]. Like the wide band gap semiconductor GaN, zinc oxide also holds lot of application potentiality in the fabrication of ultraviolet and visible light emitting devices. In fact ZnO holds better application prospects over GaN because of its hardness, large excitonic binding energy (~60 meV), wide accessibility and comparatively inexpensive development of ZnO based devices [9]. The other attracting properties of ZnO which is of interest to the research community are its high exciton binding energy of 60 meV [11], good transparency, high electron mobility, strong room temperature luminescence and very high chemical stability. The large exciton binding energy of ZnO makes it an encouraging candidate for applications in UV lasers, blue luminescent laser, varistor, photoluminescence, electroluminescence and photovoltaic devices [12-14]. It displays an intense ultraviolet light emission peak at 360-380 nm owing to the recombination of free excitons. Interesting luminescence properties of ZnO make it useful in many optoelectronic applications like laser diodes, UV light emitting diodes etc. [15, 16]. Other promising applications of ZnO pertain to chemical and gas sensor, photocatalysis, low voltage phosphorescence, conductive transparent electrodes used in solar cells and electronic flat panel displays etc. [17-20]. It has huge applications in cosmetic and medical trades for its UV absorbing properties. The occurrence of surface defects likes oxygen vacancies and zinc interstitial in ZnO nanostructures exhibits visible region fluorescence emission [21]. The color of emission can be changed with modification in the surface [22] and variation in the size of nanoparticles [23]. Metal oxide electrodes are highly useful in solid state solar cells and dye-sensitized solar cells [24]. ZnO is highly conductive and transparent in visible region and have applications in heterojunction photovoltaics [25, 26]. The polar Zn–O bonds and non-centro symmetric crystal structure of the wurtzite ZnO promotes the ferro [27, 28], piezo and pyro electricity in the samples. The ferromagnetic behavior observed in ZnO is associated with the occurrence of various defect states like oxygen vacancy, zinc interstitials and zinc vacancies in the sample [29]. The multiferroic nature of ZnO explores it as an efficient applicant for spintronic and multiple state memory devices. These outstanding physical properties and tremendous application potentiality of ZnO are motivating factors behind device miniaturization involving the compound. A huge effort have been made by researchers on the synthesis and characterization of ZnO and doped ZnO nanomaterials aimed at the improvement in the desired material properties and their device applications. The structural, optical, electrical and magnetic properties of ZnO can be modified fruitfully by incorporation of different metals and non-metals in the host ZnO.

Low efficiency of pure ZnO nanoparticles in visible and near infrared regions makes it unsuitable for use in photocatalytic devices. However, doping these nanoparticles with suitable metal /non-metal ions improve the photocatalytic activity of nano ZnO [30-32].

1.2. Diluted magnetic semiconductor:

The extension of the properties of ZnO nanoparticles by the incorporation of transition metal (TM) ions like iron, nickel and cobalt has attracted huge research attention [33, 34]. The doping of transition metal ions in ZnO matrix develops room temperature ferromagnetism (RTFM) in addition to the change of band gap and light absorption properties in the host material. Materials possessing semiconducting and magnetic properties simultaneously, are grouped under a new class of materials named as dilute magnetic semiconductors (DMS) [35, 36] and are in high demand in the electronic industry. TM doped ZnO nanoparticles are significant because of their capability to modify both the conducting and magnetic properties. The room temperature magnetic behavior of DMS materials promotes promising application of the material in the spintronic devices [37]. The roots of RTFM in TM doped ZnO nanoparticles are yet to be resolved. As such, there is a growing interest in both theoretical and experimental research for understanding the RTFM and other semiconducting properties of TM modified ZnO nanoparticles.

1.3. Historical introduction of ZnO:

In recent years the data collections in many scientific reports with the key word ZnO within various research areas including nanotechnology, nanoengineering, nanomaterial and environmental sciences. In the ancient age, purified ZnO was used for fabrication of the first brass-metal and the medical equipment. In the last few decades, there is a growing attraction to ZnO powder as a fascinating industrial manufacturing chemical and a pigment as white paint. Forever one hundred years or more, polycrystalline bulk ZnO has also been preferred in various applied fields such as gas sensors, electronic materials, cosmetic and dye-sensitive industry [38, 39]. The passionate attention in this material took place in the 1920s for its attracting semiconductor properties. During 1950s, the focus of the researchers was devoted to the growth of bulk ZnO and its applications [40]. In 1960s, bulk ZnO and also its thin film have been broadly investigated for potential applications as sensor and catalyst [41]. Since 1990s, there is a growing interest on the preparation of ZnO nanostructures through different growth route [42, 43]. Since 2000, research interest in the synthesis of the high quality ZnO nanomaterials for the ZnO assisted electronic, optoelectronic, spintronic and multiferroic devices have led to hundreds of quality papers and patents every year.

1.4. Basic knowledge about ZnO:

1.4.1. Basic physical parameters of ZnO:

ZnO is characterized with the following physical parameters [9, 44]

- Molecular weight = 81.37 g/mol.
- Color of pure microcrystalline zinc oxide is white.
- Lattice constants: a = 3.2495 Å, c =5.2069 Å
- Band gap at 300K is 3.37 eV
- Density = 5.67526 g/cm^3.
- Melting point of zinc oxide at atmospheric pressure is over 1200 ^{o}C. Under high pressure it is nearly about 1975 ^{o}C.
- ZnO possess the vapor pressure (1500 ^{o}C) of 12 mm Hg.
- Refractive index of ZnO: w = 2.008, e = 2.029.
- Specific heat = 0.125 cal/g ^{o}C.
- Exciton binding energy of ZnO is 60 meV.

1.4.2. Structure of ZnO:

ZnO under different growth and environment conditions crystallize in one of the three different types of crystal structures viz. hexagonal wurtzite (figure 1.1), cubic zinc blende and rarely perceived cubic rocksalt [9]. At ambient conditions, hexagonal wurtzite phase of ZnO with $P6_3mc$ space group symmetry is thermodynamically stable. The ionicity of wurtzite ZnO is inherent at the borderline between covalent and ionic semiconductor.

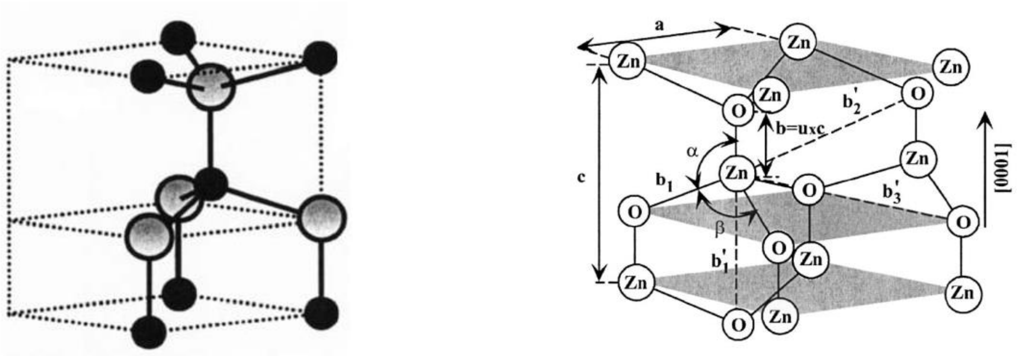

Fig. 1.1. Schematic representation of ZnO wurtzite crystal structure. The black spheres present O atoms and gray spheres present Zn atoms. Lattice constants a and c are in basal plane and basal direction respectively; u is the bond length (0.375 in ideal crystal), α and β are bond angles (109.47° in ideal crystal [9].

Wurtzite structure consists of a hexagonal unit cell with the ratio of lattice parameters $c/a = \sqrt{(8/3)} = 1.633$. Schematic representation of wurtzite ZnO structure is presented in figure 1.1 [9]. The wurtzite structure is comprised of two interpenetrating hexagonal-close-packed sublattices, where each sublattice involves with one type of atom. The two sublattices are displaced with respect to their positions towards the three fold *c*-axis by an amount $u = 3/8 = 0.375$ [45] (for ideal wurtzite structure). The u parameter is defined as $u = \left(\frac{1}{3}\right)\left(\frac{a^2}{c^2}\right) + \frac{1}{4}$. Each sublattice is composed of four atoms in a unit cell. Every zinc atom is connected to four atoms of oxygen and vice versa, which are situated at the edges of a tetrahedron.

1.4.3. Optical properties of ZnO:

Absorption and emission properties of semiconductor depend on both intrinsic and extrinsic effects. Fundamental optical absorption or emission takes place due to transition of electrons from valence band to conduction band. In ZnO structure intrinsic transition also includes excitonic effects because of columbic interaction. Extrinsic effects originate from the dopants or defects, which influence both the absorption and emission processes. Band gap of a semiconductor can be tuned through incorporation of another metal or non-metal.

Transition metal doping in ZnO matrix generates localized electronic states in the band gap of the semiconductor and therefore influence the optical and other properties of the material. Some literatures have reported the optical properties of group III element (Al, In, Ga etc.) doped ZnO [46-48]. Doping ZnO with group II elements (Ca, Cd and Mg etc.) is reported to tune the band gap energy and also modify the intensity of UV luminescence [49]. Tuning of optical band gap is also related to grain size. Raman scattering of Al-doped ZnO nanoparticles was discussed by Kadam et al. and Lo et al. [50, 51]. Thickness dependent alteration of band gap energy with Al-modified ZnO thin film fabricated through spray pyrolysis was studied by Lai et al. [52]. In 2009 the structural, optical and electrical characterizations of Cr-modified ZnO micro particles were reported by Singh et al. [53]. The effects of Ni, Co and Fe substitution on the band gap of ZnO are investigated in this report.

The defects in ZnO crystals are mainly due to the creation of vacancies, interstitials and antisites. Generally, the formation energy of oxygen vacancies (V_o) is lower than the formation energy of zinc interstitial (Zn_i). Recently the green emission in ZnO is accredited to many deep level defects like V_o and zinc vacancy (V_{Zn}) [54-56)]. The recombination between the energy level of Zn_i to Zn is the reason of blue emission [57]. Normally, the defect levels of zinc interstitial located at 0.22 eV below the conduction band creates visible emission due to the recombination of Zn_i and various deep level defects like oxygen interstitials and the vacancies of oxygen and zinc [58]. The orange red emission in ZnO is generally originated due to oxygen interstitials defect level situated at 2.28 eV below the conduction band [59]. Transitions ascribed to various defect levels are presented in the figure 1.2 [59-61]. Despite various literatures the mechanism of visible band of luminescence spectra is yet to be resolved clearly. The defect mediated visible emission such as green, yellow and blue radiations in doped ZnO have also been reported [62-66]. This research work reports the strong excitonic UV emission of Ni, Co, Fe, Mg and Nd doped ZnO nanoparticles and their potential application in UV light emitting devices.

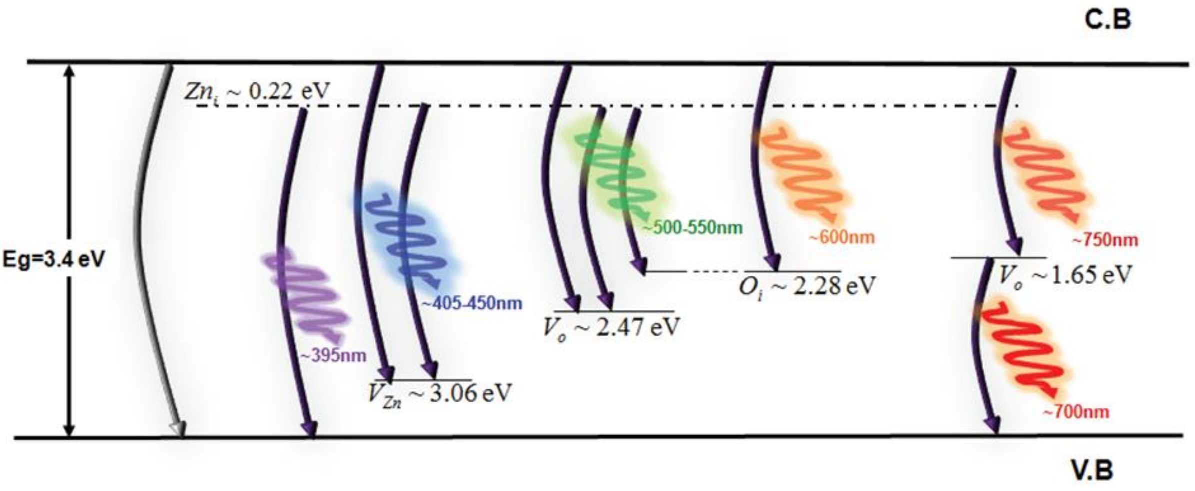

Fig. 1.2. Transitions ascribed to various defect levels in ZnO [59-61].

1.4.4. Photocatalytic activity of ZnO:

ZnO with large exciton binding energy, high redox potential, superior physical and chemical stability and nontoxicity draws a wide attention for photocatalytic activities compared to other semiconductor photocatalysts [67, 68]. ZnO has an effective photosensitive property for degradation of harmful pollutants and dyes [69, 70]. ZnO is a favored photocatalytic activist over TiO_2 owing to larger quantum efficiency, absence of any secondary environmental pollution [71, 72] and lower cost. However, pure ZnO has some shortcomings as a photocatalytic material for its activation requires high energy UV light resulting in low yield efficiency in the visible and near infrared regions. Further, the fast recombination rate of the photo-generated electron-hole pair in case of pure ZnO restricts the economic sustainability [73, 74]. These limitations could be overcome by inducting intrinsic defects through incorporation of transition metals, non-metals and rare earth elements in the ZnO matrix [75-77].

Mn-doped ZnO nanosystem has been discussed for better photocatalytic efficiency [78-80]. Ni-doped ZnO nanosized composites also explored for improved photocatalytic activity [81, 82]. The degradation of 1, 2-dichlorobenzene (DCB) and methyl orange (MO) by Fe-doped ZnO system has been analyzed by Zhang et al. [83]. Mg^{2+} with similar ionic size as that of Zn^{2+} [84] is considered as a potential dopant in host ZnO for enriched photocatalytic activities. Several reports have discussed on the growth techniques of Mg-doped ZnO nanostructures and their optical properties [85-87], but studies on photocatalytic activity of this compound are very rare. In 2013 degradation of 4-chlorophenol by Mg-doped ZnO nanoparticles was discussed under UV light irradiation [88]. Photocatalytic degradation of RhB assisted through UV light using Mg-doped ZnO nanoparticles was reported in 2015 [73]. In literature, just a single report has crossed our attention on the sunlight-driven photocatalytic degradation of methylene blue (MB) by Mg-doped ZnO nanoparticles [85]. Rare earth (RE) ions are efficient luminescence centers in doped ZnO nanomaterials [89-91]. Neodymium, a rare earth group element has enriched optical properties for potential application in various optoelectronic [92] devices. Recently Nd^{3+} ion doped ZnO nanoparticles were reported to act as efficient photocatalytic agent for destruction of harmful contaminant [93, 94]. In 2014 degradation of methyl orange under UV light irradiation by Nd-doped ZnO nanoparticles was conducted successfully by Zhao et al. [95]. In the same year, the photocatalytic deprivation of Congo red with the help of Nd-doped ZnO was analyzed by Zhang et al. [96]. A report has been noticed on UV light irradiated degradation of methylene blue (MB) by 0.5 and 1% Nd^{3+} doped ZnO nanoparticles [93].

Photocatalytic degradation of methylene blue under sunlight irradiation using self-assembled Mg-modified ZnO nanomaterials synthesized through a very simple chemical precipitation technique has been analyzed as a part of this work. We also report the result of a study on the sunlight irradiated photocatalytic degradation of MB by Nd^{3+} ion (3% -15%)

doped ZnO nanopowders synthesized through easy and inexpensive chemical precipitation method.

1.4.5. Magnetic behavior of ZnO based materials :

The source of ferromagnetism in case of ZnO based DMS is still not clearly resolved. Several literatures assigned the magnetism in these DMS to many factors like that induced by defects, presence of magnetic secondary phases, metallic clusters or other unwanted impurities [97-99]. While pure ZnO in its bulk form is diamagnetic in nature, many investigations in nanocrystalline ZnO have reported to observe ferromagnetism [100-102]. Some researchers have assigned the magnetism in TM doped ZnO systems to the occurrence of parasitic phases and extrinsic impurities which are sensitive to the preparation techniques and the environmental conditions [103]. Till now various studies have dealt on the magnetic properties of TM (Fe, Cr, Mn, Ni, Co etc.) doped ZnO [104-107]. While some researchers assign the FM in TM doped ZnO to dopant or intrinsic defects, some others assign the phenomena to cluster formations or extrinsic defects (such as oxygen vacancies). There are also reports on the superparamagnetic and paramagnetic nature of these samples [108, 109]. These debatable discussions on the magnetic properties of these materials suggest that the characterizing parameters are very sensitive to growth techniques. There are strong arguments favoring magnetic interactions between the TM ions as the source of magnetism [110-112]. Earlier studies discussed that the magnetic properties of ZnO are originated from exchange interactions of local atomic moments and *sp*-band electrons and in effect through the formation of bound magnetic polaron [113]. Some studies on thin films and nanosystems of Fe-doped ZnO suggest the increased carrier density as the intrinsic source of magnetism [114, 115]. Ferromagnetic ordering has been detected in low-dimensional system through hole-mediated exchange at low transition temperature ($T_c < 2$ K) [116]. In 1990s a technological innovation in the field of DMS has been achieved when ferromagnetism was detected in Mn-doped InAs below the temperature of 35 K [117]. Later, the ferromagnetic nature of Mn-modified ZnO nanomaterials was analyzed according to Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction by Cong et al. [118]. The magnetism in the cobalt doped ZnO nanoparticles as DMS was examined by many researchers [119, 120]. Room temperature ferromagnetism (RTFM) was observed by Sharma et al. (2003) in Mn-modified ZnO systems [121]. Afterwards several researchers have reported RTFM in various transition metals doped ZnO synthesized through different preparation techniques [122-124]. Strong arguments were forwarded linking the ferromagnetic nature in TM doped metal oxide nanomaterials with the oxygen vacancies [125, 126]. The room temperature ferromagnetism in cobalt and nickel doped ZnO nanoparticles prepared through an alcoholysis ester elimination method is studied vis. a vis. the oxygen vacancy [127]. Again manganese and nickel doped self-aggregated ZnO nanoparticles have reported to exhibit tuned optical and magnetic properties [128, 129]. Cobalt, manganese also have been incorporated to different ZnO structures such as nanorods, nanowires etc. with different doping concentration [130]. A large magnetization value of ZnCoO nanosystems was reported to be achieved through ball milling method by Pal et al. [120] and was discussed on the basis of bound magnetic polaron (BMP) model. Nickel doped ZnO DMS is another promising candidate for the study of magnetism with transparent properties, applicable to the field of optical communication as integrated circuit and short wavelength [131]. Ferromagnetism in various nanostructures such as Ni-doped ZnO nanotubes, nanorods [132], thin films [133], nanowires [134] and quantum dots have been reported with Curie temperature extending to (T_c) 350 K [135, 136]. The origin of RTFM developed in Ni-doped ZnO film was argued on the basis of defect states by Liu et al. [137]. Like Mn, Co and Ni doped ZnO, Fe-doped ZnO nanomaterials are also a potential DMS system [138]. Some of the models employed to explain the magnetic interactions in the TM doped ZnO nanosystems are listed below.

1.4.5.1. Description of models significant for magnetism in DMS:

- **Carrier mediated Ruderman-Kittel-Kasuya-Yosida Model:**

The RKKY model [139] is based on the magnetic interaction with localized and delocalized single magnetic ion and conduction band electrons respectively. Owing to this interaction, magnetization is induced in the conduction electrons near to the magnetic ion. Consequently the magnetic ordering of neighboring ions gets altered through the oscillatory polarization decaying with distance from the magnetic ion. Thus the magnetization is the result of super exchange interaction of indirect pattern with two magnetic ions placed on nearest or next closest neighbors. This pairing yields a parallel for ferromagnetic and/or anti-parallel for antiferromagnetic orientation of moments reliant to separation with the interacting atoms. RKKY model is suitable for application to systems with highly concentrated delocalized carriers in the host matrix.

- **The Mean Field Zener Model:**

This theoretical model is accredited to the model of Zener [140] and RKKY interaction [141]. Here, the RKKY like interaction is formed by the delocalized hole carriers along with localized TM ions to yield ferromagnetism. The theory is pertinent to the complex valence-band system of zinc-blende semiconductors and encompasses the aspect of spin-orbit coupling to determine the Curie temperature (T_c) and easy axis in *p*-type ferromagnetic semiconductors. The hole mediated exchange [142] is reported to be effective indicating stabilization of high T_c ferromagnetism in *n*-type ZnO.

- **The Double Exchange Model:**

The ferromagnetism in some manganite materials is analyzed on the basis of Zener's double exchange mechanism [140]. This interaction arises due to hopping of electrons of two neighboring TM ions. In DMS materials, exchange interaction between the TM ions mediated through the crystal field results in the splitting of 3*d* levels to a lower and higher energy doublet and triplet states respectively. Spin-up (↑) and spin-down (↓) states are also found to be splitted according to exchange splitting. In Co-modified ZnO material, it is proposed that the spin-up (↑) Co 3*d* states and oxygen 2*p* states are strongly hybridized [143, 144]. Moreover the spin-down states are placed near to the conduction energy band of host ZnO. Ferromagnetic ground state has been favored due to the hopping from one ion towards other as parallel alignment between magnetic moments of neighboring Co ions and electrons of the partly filled 3*d* orbitals.

- **Bound Magnetic Polaron Theory:**

Bound magnetic polaron (BMP) approach has been employed by several researchers to elucidate the ferromagnetic ordering of TM modified ZnO. BMP is a consequence of coupling of charge carriers (electrons or holes) bound to doped ions through exchange interactions [145]. These interactions are liable for parallel or anti-parallel ordering of carriers reliant to the system. The energy of parallel & anti parallel alignments are different resulting in a non-zero spin orientation energy. The lowest energy of the resulting system can be achieved by parallel arrangement of ions. The *s-d* exchange energy becomes greater than K_BT at low temperatures, so ferromagnetism is originated by mutual configuration of ions and carriers. BMP can assist the magnetic ordering to a temperature on the basis of interactions between collective atomic spins and the localized charge carriers. The total exchange has been derived according to the polaron-pair model by Durst et al. [146] allowing the interaction between a pair of BMPs. A schematic pattern of the magnetic polaron model is presented in figure 1.3.

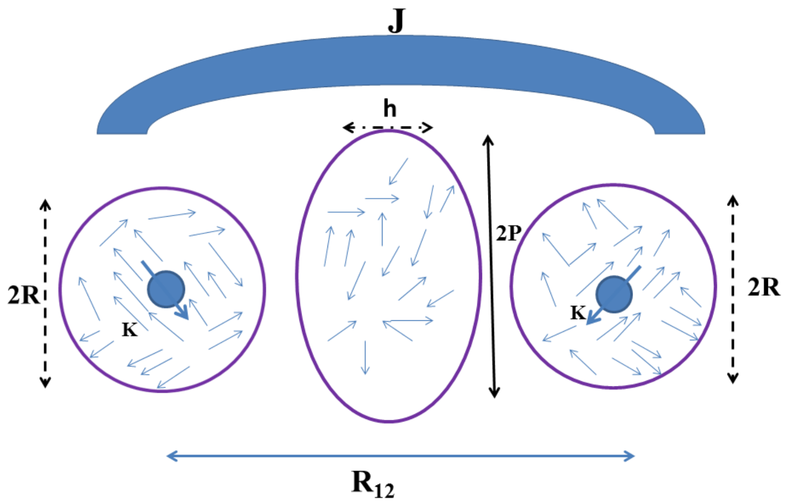

Fig. 1.3. Schematic presentation of magnetic polaron model.

In the presence of large donor bands, weak *s*-*d* interactions results the creation of BMPs in the collective phase preferably at low temperatures. Rather at the time of highly localized valence energy bands are implicated, the *p*-*d* interaction becomes efficient to maintain collective phase at low as well as high temperatures.

A schematic interaction in the oxides is displayed in figure 1.4 [147], where an electron source coming from oxygen vacancies as defect. With the increase in the number of the electrons having orbital size comparable to Bohr radius, interaction between these electrons and the magnetic ions positioned within their orbit becomes appreciable. If the orbit encompasses sufficient number of magnetic spins, then complete spin polarization is possible. Again, the atomic magnetic moments yield ferromagnetic ordering by carrier mediated indirect exchange interaction.

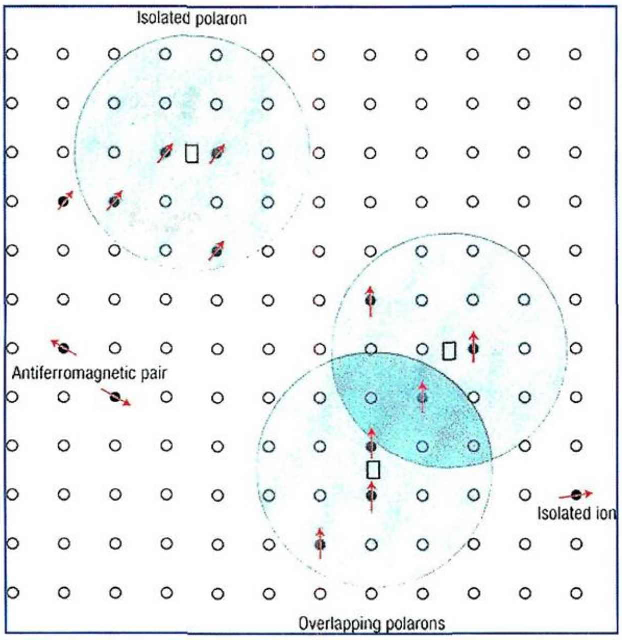

Fig. 1.4: Schematic image of magnetic polarons in a semiconductor lattice. Cation sites and unoccupied oxygen sites are displayed by small circles and squares respectively [147].

The ME effect is the basis of manipulating and collectively controlling the two degrees of freedom for DMS material. We have not come across any report on magnetoelectric (ME) effect of TM doped ZnO nanocompounds. In this work, ferromagnetic, ferroelectric properties and mutual coupling between magnetic and electric field on TM doped ZnO nanoparticles have been discussed. In recent times, the ferromagnetic property has been perceived in some non-magnetic element such as Li and Mg doped ZnO [148-150]. Although some literature have studied on the ferromagnetic properties of Mg-doped ZnO, yet the multiferroic property and magnetoelectric coupling of this compound has not been studied. The magnetic, ferroelectric and ME coupling properties of Mg-doped ZnO synthesized through simple chemical precipitation method is included in this report.

1.5. Motivation & object of study:

As explained above, zinc oxide and its modified nanomaterials are extensively applicable in various devices due to their structural, optical and multiferroic properties. The doping of various transition metal ions (Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}), the rare earth element ions like Nd^{3+} and other metallic ions like Al^{3+} and Mg^{2+} in host ZnO has created interest among the researchers [151-154] for their multifarious application potentialities. Individual metal ions with their specific size, charge and spin arrangement modify/enhance the electric, magnetic, optical and photocatalytic properties of the host material. The specific requirements for diverse applications grow a durable interest in improvement of growth technique of ZnO nanostructures with controllable size and shape. The various growth routes considered for fabrication of ZnO nanostructures are based on physical vapor deposition, chemical vapor deposition, solvothermal synthesis, microemulsion method, pyrosol, sol-gel process and chemical precipitation techniques [155-160]. The preparation method engaged for fabrication of ZnO nanocomposites should facilitate not only ZnO nanoparticles with particular size and shape, but also confide on experimental circumstances, low materials cost and non-sophisticated equipment. The main drawback in microemulsion method is very low product in return. The average particle size of the ZnO nanoparticles prepared through solvothermal [157], microemulsion [158] and pyrosol [159] methods are reported to be around 30-70 nm, 100 nm and 500 nm respectively. The energy consumption in the solvothermal method is quite high. Out of these techniques of nanomaterial synthesis, the chemical precipitation method is an advantageous method because it helps to accomplish ZnO nanocompounds with specific sizes (10-30 nm) and shapes [160]. Sol-gel method is also an easy technique to produce nanoparticles with nearly 30 nm sizes. Chemical precipitation and sol-gel techniques have a considerable appeal because of its low synthesis cost, easy manipulation and large scale production facilities of ZnO nanostructure. These methods also have some advantages as regards to low energy requirement for processing and affords a template free synthesis method effectively inhibiting any incorporation of impurities to the ZnO matrix [161]. In this work, we present an easy, inexpensive, low temperature growth technique to synthesize transition metal (Ni, Co, Fe) doped ZnO nanoparticles with controllable size. The doped ZnO nanoparticles were studied to assess the optical, electrical and multiferroic properties.

The main focus of this research effort is to develop self-assembled doped ZnO nanoparticles for spintronic and multiferroic applications. We are thus motivated to study the optical, magnetic, ferroelectric and ME coupling properties of doped ZnO nanoparticles synthesized through simple chemical precipitation and sol-gel techniques using hydroxyoxalate type precursors.

Doping of rare earth (RE) ions in host matrix generally enhances the optical properties and act as efficient luminescence centers [89-91]. Further, as explained in section 1.4.4, the ZnO nanoparticles doped with rare earth and other metallic elements are fast emerging as efficient photocatalyst for degradation of dyes, for its ability towards tuning the band gap depending on the dopant ion and their concentration, large quantum efficiency and absence of any secondary environmental pollution. It is worth pointing here that water pollution caused from various industrial effluents is a major global complication [162-164]. A remarkable amount of azo dyes, non-fixed dyes and inorganic salts remain present in the waste water of textile industries [165]. This waste water can be prevented from the pollution of dyes through photocatalytic effect [166]. Presently, titanium oxide (TiO_2), reduced graphene oxide (RGO), zinc oxide (ZnO), tungsten oxide (WO_3) and tin oxide (SnO_2) are being in use as photocatalysts. Recently, ZnO nanoparticles doped with Nd^{3+} ion deport itself as an attracting photocatalytic agent for removal of the pollutant from waste water [93, 94].

Establishment of Mg and Nd doped ZnO as an efficient photocatalyst for degradation of various organic and inorganic pollutants coming from industrial effluents is also an important part of this work. The photocatalytic activities of Mg and Nd doped ZnO nanoparticles under sunlight irradiation have been explored.

In chapter 2, we briefly explain the various synthesis techniques used for preparation of doped ZnO with their merits and demerits. In this chapter also a brief outline of the different structural, optical, electrical and multiferroic characterization techniques used in this project have been presented.

In chapter 3, 4, 5, 6 and 7 we have reported our investigation on Ni, Co, Fe, Mg and Nd doped ZnO nanoparticles respectively. The study for each of the doped samples is carried out for five different doping concentrations of 3, 6, 9, 12 and 15%. The XRD, EDX and FTIR studies for structure and chemical compositions involve in this work. The surface morphology, particle size and shape have been studied by TEM and HRTEM characterizations. The absorption and emission spectra have been used to investigate the optical properties of pure and doped ZnO nanoparticles. The electric, magnetic and magnetoelectric coupling have been studied through dielectric, P-E, M-H and ME measurement for the doped samples. In case of Mg and Nd doped ZnO species, study has been carried out on the photocatalytic activity for each of the different doping concentrations. Finally, we have summarized our findings in Chapter 8.