Chapter-1

Introduction
Introduction

Metals and their compounds with the nonmetals such as oxygen, nitrogen, selenium, tellurium are the materials that have been scientifically and industrially exploited for the last several decades due to the fact that they have a known crystal structures and structure dependent properties [1]. These materials, in general, belong to seven crystal systems and 14 Bravais lattices. Properties such as electric, magnetic, optical, catalytic, sensor, etc. of such materials no doubt depend on the crystal systems and lattices to which they belong, but defects and non-stoichiometry play a crucial role in deciding a particular property [2]. However, all these critical parameters and the properties can be realized only through well strategized synthetic procedures, heat treatments etc. and hence tailoring of the materials is of prime importance in the field of solid state chemistry research. Although the large scale production may involve chemical engineering aspects, the laboratory scale synthesis and characterization are the starting point which allows one to do systematic investigations on any system that one chooses. There are several thousands of materials of industrial significance that find applications as pigments, catalysts, sensors, electronic, optical and magnetic components in electronics industry, structural materials in construction and automobile industry etc. and the list is very exhaustive. There are equally very large number of materials already synthesized and characterized at laboratory scale by
various researchers which may find in future wider applications. The research activity is thus a continuous process. It is more so because material scientists have to their disposal entire periodic table to choose metals and nonmetals. In our laboratories for the last 3 decades, we have been investigating the synthesis and characterization of electric, magnetic and catalytic properties of systems such as metal oxides [3-16] of spinel structures, viz \( \gamma\text{-Fe}_2\text{O}_3 \), ferrites, \( \text{MFe}_2\text{O}_4 \) \((M=\text{Mg/Mn/Ni/Zn})\), perovskites structures, viz \( \text{LaMO}_3 \) \((M=\text{Co/Ni})\) and doped \( \text{LaM'}\text{MO}_3 \) \((M'=\text{Sr/Ba/Ca})\). In the present research work, we are investigating a new systems \( \text{CuFe}_2\text{O}_4 \) and potassium (K) doped \( \text{CuFe}_2\text{O}_4, \text{SnO}_2 \), and old systems such as the \( \gamma\text{-Fe}_2\text{O}_3 \) and Li doped \( \gamma\text{-Fe}_2\text{O}_3, \text{Mn(Zn)Fe}_2\text{O}_4 \), \( \text{La(Sr)CoO}_3 \), \( \text{La(Sr)MnO}_3 \) for their likely catalytic and sensor applications. Also, we have taken up other systems such as \( \text{TiO}_2 \) and \( \text{ZnO} \) for their likely photocatalytic applicability.

1.1. Background

Monitoring and controlling environmental humidity, gases such CO, \( \text{NO}_x \), \( \text{H}_2\text{S} \), \( \text{NH}_3 \), \( \text{SO}_2 \), \( \text{Cl}_2 \), volatile organics, is receiving wider attention, mainly for comfort and industrial processes.

In recent years inorganic metal oxides like \( \text{ZnO} \), \( \text{TiO}_2 \), and \( \text{SnO}_2 \), \( \text{CuFe}_2\text{O}_4 \), gamma iron oxide, \( \gamma\text{-Fe}_2\text{O}_3 \), Mn-Zn-ferrite, etc. are found to be good catalytic, photo-catalytic and gas-sensitive materials. For detecting \( \text{H}_2\text{S} \) down to ppb levels at room
temperatures (RT) ZnO finds [17] the sensing activity, while the gas sensing property of SnO$_2$ can be enhanced by doping with copper [18]. High sensitivity towards H$_2$, CO, and liquefied petroleum gas (LPG) at optimum temperatures have also been found for nanosize resistor SnO$_2$ [19]. SnO$_2$ also finds sensitivity towards ethanol [20] at 1075 to 500 ppm level.

The tetragonal CuFe$_2$O$_4$, showed a good response to alcohol [21]. The spinel CuFe$_2$O$_4$ and that promoted with Li/K/Cs/V/Pt have been effective in catalytic removal of NO$_x$ and diesel soot [22-24]. Mn-Zn-ferrite shows high humidity sensitivity even at the relative humidity (RH) of 1.54% [25]. Conducting properties of most of the spinels such as MgFe$_2$O$_4$ [26] have been made use in humidity sensitivity. Sensing activity of $\gamma$-Fe$_2$O$_3$ doped with Cd for LPG, hydrogen and CO [27], Pt-doped for alcohol [28], Ag-doped for H$_2$ and LPG [29], Zn-doped for acetone/ethanol in presence of methane, H$_2$ and CO [30] indicates the versatility of this spinel. Most of the spinels have sensitivity for various gases and the selectivity for a particular gas becomes critical as it is observed in an exhaustive study of the systems such as CuFe$_2$O$_4$, CoFe$_2$O$_4$, ZnFe$_2$O$_4$ and NiFe$_2$O$_4$ for gases such as LPG/CO/Cl$_2$/H$_2$/NH$_3$/H$_2$S/O$_2$/CH$_4$ [31].

Rutile TiO$_2$ based humidity sensors are studied vigorously as it is likely to show better sensitivity because of its hydrophilic property. However, since it shows hysteresis in humidity sensitivity,
the addition of iso-structural SnO\textsubscript{2} of fairly good electrical conductivity to TiO\textsubscript{2} minimized the hysteresis effect and improved activity [32]. Alkali doped Anatase TiO\textsubscript{2} too showed improved humidity sensitivity [33]. Titania, TiO\textsubscript{2}, crystallizes in three different structures: Anatase, brookite and rutile and only the last one is the most stable phase, while the remaining two are meta-stable phases. Among various semiconducting oxide materials for controlling air quality, TiO\textsubscript{2} is one of the most widely used in gas sensing applications. In reactions involving titania, oxygen vacancies are one of the major advantages. Additives to this oxide further enhances conducting properties and hence the sensing activity. Pt-doped nano-size titania found to highly sensitive for NO\textsubscript{2}, CO and CH\textsubscript{4} [34].

Since the discovery of the effect of photosensitization of the TiO\textsubscript{2} electrode on the electrolysis of water into H\textsubscript{2} and O\textsubscript{2} by Honda and Fujishima in 1972 [35], photocatalysis by TiO\textsubscript{2} semiconductors have received much attention, with the final aim of efficiently converting solar light energy into useful chemical energy. Apart from solving energy crisis the photo-catalyst has potential to oxidize pollutants, airborne and waterborne, into harmless compounds. Its wide band gap necessitates the use of ultraviolet (UV) radiation to excite the electrons from the valence band to the conduction band, leaving holes in the valence band. These electron and hole pairs can then initiate the redox reactions with the molecular species
adsorbed on the surface of the catalyst [36]. Although TiO$_2$ is one of the choicest photo-catalysts, ZnO is another widely investigated material for photocatalytic degradation of organic pollutants [37]. Variety of metallic additives have been found to improve the photo-degradation capability of the semi-conducting oxides by modifying the electronic state of these oxides. However, as only 3-4% of the solar energy that reaches the earth crust consists of the UV radiations the photo-catalysts can not function to their fullest capacity, and, therefore, many photo-degradation set-ups are required to be equipped with expensive UV irradiators. In order to make use of the major portion of the solar energy near UV region there are hectic activities to prepare UV-Visible light sensitive materials. Metals and especially the non-metals such as nitrogen incorporations in the TiO$_2$ [36, 38-44] and ZnO [45-46] have been found to alter the band gap and in turn make them visible light sensitive photo-catalysts.

1.2. Organization of Thesis

**Chapter I:** deals with the literature pertaining to the systems: spinels such as $\gamma$-Fe$_2$O$_3$, Li doped $\gamma$-Fe$_2$O$_3$, CuFe$_2$O$_4$ and K doped CuFe$_2$O$_4$, Mn(Zn)Fe$_2$O$_4$; perovskites: La(Sr)CoO$_3$ and La(Sr)MnO$_3$, anatase TiO$_2$ and N / Fe doped TiO$_2$, ZnO, and SnO$_2$. Aim and methodology of the research work are being clearly spelt out in this chapter.
Chapter II: highlights the different methods of synthesis and characterization of the systems.

Chapter III: describes the sensor properties of the spinels, perovskites and SnO₂.

Chapter IV: evaluates the catalytic and photocatalytic activities of γ-Fe₂O₃, TiO₂ and ZnO.

Chapter V: Summarizes the overall results and conclusions.

References: Literature cited are compiled in this section.

1.3. Structure property relations: Literature survey

1.3.1. Spinel system.

1.3.1.a. Gamma Iron oxide (γ-Fe₂O₃).

Gamma ferric oxide, γ-Fe₂O₃, is a vacancy ordered defect spinel similar in structure to the inverse spinel magnetite, Fe₃O₄. A unit cell structure of this ferrous-ferric Fe₃O₄ is written as, (Fe³⁺)₈[Fe²⁺₈Fe³⁺₈]O₃₂, where ( ) and [ ] represent, respectively, the tetrahedral and octahedral sites. On controlled oxidation of the spinel Fe₃O₄ the Fe²⁺ ions get oxidized to Fe³⁺ and for every 3Fe²⁺ that oxidizes to 2Fe³⁺ there occurs one vacancy, □, resulting into γ-Fe₂O₃, (Fe³⁺)₈[Fe³⁺₈Fe³⁺₄+1/3□₈/₃]O₃₂. In the formation of the gamma iron oxide it was well considered that to stabilize the phase the presence of moisture is essential and this in turn allows the moisture to retain in its lattice in the form of protons. Any attempt to remove the moisture in the gamma ferric oxide leads it to
transform into thermodynamically stable phase, \( \alpha\)-Fe\(_2\)O\(_3\). The
proton containing gamma ferric was visualized based on the lithium
ferrite, LiFe\(_2\)O\(_4\), (LiFe\(_5\)O\(_8\)), (Fe\(^{3+}\))\(_8\) [Fe\(^{3+}\)\(_{12}\)Li\(^+\)\(_4\) ]O\(_{32}\) and hydrogen
ferrite, HFe\(_5\)O\(_8\), (Fe\(^{3+}\))\(_8\) [Fe\(^{3+}\)\(_{12}\)H\(^+\)\(_4\) ]O\(_{32}\) and the \( \gamma\)-Fe\(_2\)O\(_3\) may have the
chemical composition in between the hydrogen ferrite and (Fe\(^{3+}\))\(_8\)
[Fe\(^{3+}\)\(_{12}\)Fe\(^{4+}\)\(_{12}\) ]O\(_{32}\) of general formula, H\(_{1-x}\)Fe\(_{5+x}\)O\(_{32}\). Electrical
conductivity measurements in inert atmosphere and a known
partial pressure of moisture indicated [47] easy removal of the
moisture and reintroduction of the same. This causes the moisture
sensitivity in the \( \gamma\)-Fe\(_2\)O\(_3\). Since the moisture sensitivity response is
electrical in nature of the semiconducting spinel \( \gamma\)-Fe\(_2\)O\(_3\), the
adsorption of moisture seems to be chemisorption involving
electrons in the process. If so the oxide may also be a good sensor
for various reducing gases.

Literature reveals a wide variety of materials to have humidity
sensitivity [48]. The materials used in humidity sensors exploiting
variations of electrical parameters are roughly classified into three
groups: electrolytes, organic polymers and ceramics. The electrolyte
humidity sensor using LiCl developed in 1938 [49] was the only
electrical moisture-sensing device available those days. However,
this showed slow response time and was unable to operate in very
humid environment or in the presence of ammonia or organic
solvents. Other materials were hence studied. Although there are
many organic polymer based materials and porous ceramics
available, they have one or other limitations. However, ceramics, in particular, have shown advantages in terms of their mechanical strength, their resistance to chemical attack, their physical and thermal stability and change of electrical properties because of water adsorption. Some of the literature cited in section 1.1 reveals the significance of semiconducting $\gamma$-Fe$_2$O$_3$ spinel as humidity and gas sensors, but the literature also indicates the importance of metal ion additives, morphology and particle sizes. Preparation methodology is another significant factor in realizing the desired chemical and physical properties.

1.3.1.b. Copper ferrite

Spinel copper ferrite, CuFe$_2$O$_4$, has cubic and tetragonal polymorphic forms. Unusual thermal, magnetic and electric properties that have been found attributed to the Jahn-Teller distortion occurring under certain conditions due to Cu$^{2+}$ ions and cation distributions on octahedral and tetrahedral sites. Oxygen deficiencies cause electrical properties. Doping with tetravalent ions such as Sn$^{4+}$ exhibited both n- and p-type and only n-type depending on the dopant concentrations [50]. Hopping conduction mechanism has been proposed on the basis of localized model electrons and additional localization has also been considered due to Sn$^{4+}$ + Fe$^{2+}$ stable pairs at B-sites (octahedral) and Cu$^{1+}$ + Fe$^{3+}$ pair at A-site (tetrahedral). The tetragonal form is an inverse spinel
in which Cu\(^{2+}\) ions occupy octahedral sites where as Fe\(^{3+}\) ions are found on both octahedral and tetrahedral sites. However, the modification of the tetragonal CuFe\(_2\)O\(_4\) by doping with potassium enhances its catalytic activity, especially in the simultaneous removal of NO\(_x\) and soot [24]. Copper ferrite is highly sensitive to heat treatment, which shows semiconducting properties. Tetragonal CuFe\(_2\)O\(_4\) is more active than the cubic one [51]. CuFe\(_2\)O\(_4\) shows a good response to alcohol [21, 52] and its sensing property can be further enhanced by additives. The sensing of gases is attributed to adsorption of reducing gases and the reaction between these gases with the adsorbed oxygen on the surface.

Several authors have reported transition from tetragonal to cubic phase but the results are not much clear. The transition temperature ranges from (415 – 633 K), which is mostly attributed to the various methods of preparation. The oxidation states of copper and its distribution in both cubic and tetragonal spinel type are found to be sensitive to the synthesis procedure, oxygen partial pressure and heat treatment [53].

1.3.1.c. Manganese zinc ferrite

MnFe\(_2\)O\(_4\) is about 80% normal and 20% inverse, but since both the cations, Mn\(^{2+}\) and Fe\(^{3+}\), are d\(^5\), the overall magnetic moment is insensitive to the degree of inversion and to heating/thermal history effects. MnFe\(_2\)O\(_4\) is expected to be
ferromagnetic with an overall moment of \( \sim 5 \) BM. An interesting
eexample of the cation site occupancies and solid solution effects
[54] is provided by the mixed ferrites, \( M_{1-x}Zn_xFe_2O_4 \): \( M = \) Mg, Ni, Co,
Fe, Mn. These ferrites are largely inverse for \( x = 0 \), i.e. \( (Fe^{3+}) [M^{2+}\Fe^{3+}]O_4 \). The zinc ferrite, \( ZnFe_2O_4 \), where \( x = 1 \), is by contrast, almost
normal at room temperature. However, the spins of the \( Fe^{3+} \) ions
on the octahedral sites of the zinc ferrite are not aligned but are
random; therefore, it is paramagnetic and shows no saturation
magnetization. On formation of the ferrite solid solution by partial
replacement of \( M^{2+} \) by \( Zn^{2+} \), a gradual change from inverse to
normal behavior is found to occur. Introduction of \( Zn^{2+} \) into the
tetrahedral sites causes \( Fe^{3+} \) ions to be displaced onto the
octahedral sites, i.e. \( (Fe^{3+}_{1-x} Zn_{x^{2+}}) [M^{2+}_{1-x} Fe^{3+}_{1-x}]O_4 \). If in the
preparation some \( Fe^{3+} \) ions are reduced to \( Fe^{2+} \) due to no proper
control of the atmosphere, a solid solution of the type, \( Mn^{2+}_{1-x}\Fe^{2+}_{x}Fe^{3+}_{2}O_4 \) may occur, which may reduce some of the magnetic
characteristics such as magnetic anisotropy parameter and
increase the permeability that is undesirable. Also the solid solution
has yet another undesirable side-effect such as enhancement of
electrical conductivity with the increase in \( Fe^{2+} \). But the enhanced
electrical conductivity is good for making use of the ferrite in gas
sensing activities as the adsorption of gases is an electronic
process.
Humidity and gas sensing

The changes in the electronic conductance of the semiconductor in the presence of adsorbed gases or water are considered due to the direct injection of carriers into either the conduction band or valence band of metal oxide semiconductors. A decrease in resistance is normally observed with the increasing humidity level in the semiconductor sensors.

The humidity results on Mn-Zn-ferrite exhibited lowering in sensitivity when sintered in vacuum as compared to the one sintered in air [25]. The vacuum sintering or firing in a reducing atmosphere enhances the electrical conductivity of most oxides due either to the production of oxygen vacancy donor states which increases the density of states in the conduction band, or to the removal of surface oxygen traps, leading to a decrease in the number of conduction electrons being trapped. The pastes of Mn-Zn-ferrite sintered in air at 400°C showed a resistance of 500 kΩ which reduced to 3 kΩ when fired at 800°C, but the same sintered in vacuum at 600°C indicated 500 Ω that then decreased to 34 Ω suggesting considerable change occurring in the electronic properties. The lowering in the humidity sensitivity of vacuum sintered Mn-Zn-ferrite can be attributed then to the changed electrical characteristics.

Reducing gas-sensing properties of ferrite compounds, MFe$_2$O$_4$, (M= Cu/Zn/Cd/Mg) to the gases such as
CO/H2/LPG/C2H5OH/C2H2 tended to decrease in the order MgFe2O4 > CdFe2O4 > CuFe2O4 > ZnFe2O4. Among these ferrites, the MgFe2O4 and CdFe2O4 were the most sensitive and selective to LPG and C2H2 [55]. Gas sensing property found not to considerably varied even metal A element deviated to some extent from the quantity defined by the general formula AFe2O4 (A= Li/Mg/Mn/Fe/Co/Ni/Zn/Pb), suggests the versatility of spinels in gas sensing capacity, in general, [US Patent 3952567]. The study of gas sensing was probed in these ferrites using the measurements of the resistivity in the relevant gas atmospheres at different working temperatures.

1.3.2. Perovskite system

Nanocrystalline perovskite, La0.8Pb0.2Fe0.8Co0.2O3, that were prepared by citrate method having p-type semiconducting property showed good sensitivity and selectivity for CO gas [56]. The orthorhombic perovskite, La1-xMgxFeO3, powder prepared by sol-gel method using citric acid indicated best response and selectivity to ethanol gas [57]. Great differences on the conduction-temperature curves of La0.92Mg0.05FeO3 based sensors between ethanol gas and air or other gas such as H2, CO, CH4 were also found. The conductance in ethanol gas decreased with temperature increase from 132-240°C. But in air and other gases such as H2, CO and CH4 the conductance increased all the time indicating that at 240°C
the conductance difference between air and ethanol was the bigger and response reached the maximum. Nanocrystalline orthorhombic LaFeO$_3$ prepared by the thermal decomposition of the La[Fe(CN)$_6$]$\cdot$4H$_2$O in the temperature range 600-1000°C showed gas response after exposure to NO$_2$ at 350°C [58]. The practical use of gas sensors are limited by the stability of the perovskite phase in reducing atmosphere at high temperatures. The sequence of stability of a series of perovskite type oxides LaBO$_3$ (B= V/Cr/Mn/Fe/Co/Ni) at 1273 K in gas mixtures of CO/H$_2$ [59] was found to be LaCrO$_3$\textgreater LaVO$_3$\textgreater LaFeO$_3$\textgreater LaMnO$_3$ \textgreater LaCoO$_3$ \textgreater LaNiO$_3$. LnMBO$_3$ (Ln = rare earth, M=alkaline earth metal and B=transition metal) were used to detect ethanol in the exhaled air in the presence of ethanol vapors. The electrical conductivity of these oxides changed drastically. This was the first example that perovskite oxides applied to the gas sensors [60]. The methanol sensing for LnCoO$_3$ and LnMnO$_3$ showed a response of 20% and relative sensitivity of 1. The activity of LnCoO$_3$ was found to be higher than that of LnMnO$_3$ [61]. Based on the classification of perovskites by Goodenough [62] the cobaltates are located on the boundary between itinerant and localized e$_g$ electrons. The catalytic properties of cobaltates are connected with the spin states and particularly with the proportion of the high spin state of the Co$^{3+}$ [63].
1.3.3. Tin oxide, SnO$_2$: a model gas sensing system

Polycrystalline SnO$_2$ have been extensively used for the production of resistors for gas sensing applications due to its high sensitivity for CO, ethanol and methane even in trace amount present in the environment. Mechanistic of gas sensing is investigated on this simple semiconducting model oxide system. When a SnO$_2$ semiconductor is exposed to air [90], the physisorbed oxygen molecules receive electrons from the conduction band and change to O$^-$ or O$_2^-$ adsorbed species. These adsorbed molecules form an electron depletion layer just below the surface of SnO$_2$ particles and form a potential barrier between particles; consequently the SnO$_2$ becomes highly resistive. The lowering of the potential barrier takes place when the adsorbed oxygen species are exposed to reducing gases, resulting in the increased conductance of the oxide. The variation of the conductance depends on many parameters such as intrinsic resistance, grain size, grain boundary barriers, detection temperature etc. TiO$_2$ also being a good humidity sensor and since SnO$_2$ is isostructural with the rutile, titania has been considered to be a good additive to improve the humidity sensitivity [32]. Among the various metal oxide additives the CuO has been found to promote the H$_2$S sensing property of SnO$_2$ [18].

Tin dioxide (SnO$_2$) is an n-type, wide band gap (E$_g$ = 3.57 eV) semiconductor. The origin of the n-type behavior is the native non-
stoichiometry caused by oxygen vacancies. SnO$_2$ is an anisotropic polar crystal, which crystallizes with tetragonal rutile structure with space group D$_{4h}$[P4$_2$/mm]. The unit cell contains six atoms, two tin, and four oxygens. Each tin atom is at the center of six oxygen atoms placed approximately at the corners of regular slightly deformed octahedron, and three tin atoms approximately at the corners of an equilateral triangle surround every oxygen atom. Thus, it is the structure of 6:3 coordination.

1.3.4. Anatase TiO$_2$

TiO$_2$ is well understood photo-catalyst for oxidizing a large variety of organic substance and also a reagent in selective catalytic reactions (SCR) over TiO$_2$ based catalysts to chemically transform NO$_x$ to environmentally innocuous dinitrogen and water [64-74]. The three polymorphs Rutile, Anatase and Brookite exist in nature. High temperature form, rutile, is thermodynamically most stable structure of titania above 800°C, while anatase and Brookite are the metastable structures which exist at lower temperatures. Both anatase and brookite undergo structural transformation to rutile structure at elevated temperatures.

Rutile and anatase are both tetragonal, containing 6 and 12 atoms per unit cell, respectively. In both structures, each Ti atom is coordinated to 6 oxygen atoms and each oxygen atom is
coordinated to 3 Ti atoms. In each case, the TiO$_6$ octahedron is slightly distorted, with 2 Ti-O bonds slightly greater than the other 4, and with some of the 4 Ti-O bond angles deviating from 90°. The distortion is greater in anatase than in rutile. The structures of both have been described frequently in terms of chains of TiO$_6$ octahedra having common edges. Two and four edges are shared in rutile and anatase, respectively. The inter atomic distances and the O-Ti-O bond angles are similar to those of rutile and anatase. The essential difference is that there are 6 different Ti-O bonds ranging from 1.87 to 2.04 Å. Accordingly there are 12 different O-Ti-O bond angles ranging from 77-105°. In contrast, there are only two kinds of Ti-O bonds and O-Ti-O bond angles in rutile and anatase. Brookite can be visualized as formed by joining together the distorted TiO$_6$ octahedra sharing three edges [75].

In 1972, Fujishima and Honda [35] have discovered the photocatalytic efficiency of splitting of water on TiO$_2$ and since then, research efforts in understanding the fundamental processes and enhancing the photocatalytic efficiency of titania have come from extensive research performed by chemists, physicists and chemical engineers. In recent years, studies are related to energy conversion such as electrochemical photolysis of water and high-efficiency solar cell system etc.. Titania has also received much attention with respect to the degradation of various environmental pollutants in water and atmosphere.
There are no limits to the possibilities and applications of photocatalytic systems for the purification of polluted air and water, as well as, safe conversion of solar light energy into chemical energy. However, TiO$_2$ semiconductors have a relatively large band gap of 3.2 eV corresponding to wavelengths shorter than 380 nm. In other words, TiO$_2$ in itself can make use of only 3-4% of the solar energy that reaches the earth, necessitating a ultraviolet (UV) light source for its use as a photocatalyst. From this point of view, TiO$_2$, which can operate efficiently under both UV and visible (Vis) light irradiation, would be the ideal for practical and widespread use.

TiO$_2$ is known as a useful photosensitive material, such as photoanodes [76] and photocatalyst [77]. However, only the UV part of the solar irradiation could be absorbed by TiO$_2$ due to its high intrinsic band gap (3.2eV for anatase and 3.0eV for rutile). For designing highly efficient and low cost photocatalytic systems, many approaches, such as doping with various transition metals cations [78] have been introduced to extend the optical absorption of TiO$_2$-based systems to the visible-light region. Though that way one can more or less extend the optical absorption, the thermal instability and increase of carrier combination centers greatly limit the performance of the transition metal dopants. [79].

On the other hand, anionic non-metal dopants, such as nitrogen (N) [41, 43], carbon (C) [80] and boron (B) [81] atoms, have also been investigated widely aimed at extending photoactivity into...
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the visible -light region. Asahi et al [43] reported that N- doped TiO₂ showed dramatic improvement over undoped TiO₂ in its optical absorption and the photoactivity activity for the visible light. Based on their analysis of the density of states, they concluded that the substitution of dopants such as N for O in the anatase TiO₂ crystal, a band-gap narrowing driven by mixing of N 2p state with O 2p states take place. However, recent experimental data seemed contradict their theoretical calculations. Irie et al [41] suggested that the visible-light response in N –doped TiO₂ might be due to N 2p states isolated above the valence – band maximum of TiO₂. Similarly, the red shift in C-doped TiO₂ had been observed by Choi et al [82] and Moon et al reported the absorption band shift towards longer wavelength in B/TiO₂.

1.3.5. Zinc oxide, ZnO

Zinc oxide is a semiconductor material with direct band-gap energy of approximately 3.2eV. Irradiation of the oxide with sufficiently energetic UV light source results in the promotion of electrons to the conduction band and the consequent formation of holes in the valence band. These photogenerated charge carriers can subsequently migrate to the surface of the oxide and initiate redox reactions with absorbed molecules in a process known as heterogeneous photocatalysis. However the quantum yield in such processes is limited due to charge carriers recombinations and
therefore, it requires a method for inhibiting such recombinations. In the well studied TiO$_2$ systems these inhibitions have been achieved by the addition of metal ion dopants. While TiO$_2$ is widely employed as a photocatalyst, ZnO is a suitable alternative to TiO$_2$, as it has a similar band gap energy, large quantum efficiency than TiO$_2$ and higher photocatalytic efficiencies [44, 83-87]. It has also been suggested that ZnO is a low cost alternative photocatalyst to TiO$_2$ for decolorization of organics in aqueous solutions. In order to make it more versatile ZnO-based materials capable of visible light photocatalysis doping with metal ions have also been tried. In order to absorb visible light, the band gap of ZnO has to be narrowed or split into several sub-gaps by doping with metal ions such as Co, Ni or Mn [88] or by doping N [89]. Basic electronic structure of N-doped ZnO (wurtzite) and ZnS/ZnSe (zinc-blend) have been investigated [46] to clarify the factors that determine the N-impurity states, either localized or delocalized ones.

The textile industry produces large quantities of highly colored effluents. These are generally toxic and resistant to destruction by biological treatment methods such as using microorganisms, which was used to decompose the sludge into smaller compounds. Azo dyes such as new methylene blue N or basic blue 24, are widely used in the textile industry. The world wide annual production of these dyes is over 7x10$^5$ tons. Over 50% of all the dyes used in industry are azo dyes. The major difficulty in
treating textile waste water is the ineffectiveness of biological processes. Traditional oxidation processes such as ozonation and chlorination are only effective in destroying some classes of dyes. As a result of these problems, advanced oxidation processes have been considered which include photocatalysis such as a combination of semiconductors, TiO₂, ZnO, Al₂O₃, WO₃ etc. and UV light.

ZnO is an n-type semiconductor with many attractive features. ZnO is considered to absorb more UV light than any other powders. In the photodegradation of new methylene blue N, ZnO was found to be better catalyst than TiO₂ and the mixture containing 85:15 (ZnO: TiO₂) showed superior catalytic activities.
1.4. Aim:

In technologies where ferrites and semiconducting oxides such as perovskites, TiO₂ and ZnO are to be used for magnetic, electric and optical applications, high density materials are generally required. Although for most applications high densities are required to achieve the desired properties, there are many applications like gas sensing, catalytic and photocatalytic for which the lower densities and high surface areas are preferred due to their fascinating electronic properties even in the less dense states. From the literature survey in section 1.3, it is apparent that the ferrite of general formula AB₂O₄, perovskites of general formula ABO₃, SnO₂, TiO₂ and ZnO show interesting gas sensing, catalytic/photocatalytic activities and there is a very clear correlation between the activities and electrical properties. For gas sensing and catalytic applications, however, the desired one single criterion is high surface area and fine particles of uniform size distributions. Hence, high temperature synthesis and sintering are not the necessary conditions and therefore, instead of ceramic techniques, one need to opt for the other techniques such co-precipitations, sol-gel, spray pyrolysis, hydrothermal etc. Among these soft chemical routes, one needs to choose easy, low cost technique. Precipitation and co-precipitation followed by thermal decompositions is the best suitable path to achieve particles of high
surface and uniform particle size distributions in the nano- to
submicron to few micron sizes.

The precipitation technique is one of the widely used methods
of preparation of metal and mixed metal oxides at much lower
temperatures and the carboxylate route has been well explored in
our laboratories for the last three decades [3-16]. However, the
modification of the oxalate precursors by hydrazine enabled us to
synthesize the oxides at still lower temperatures with improved
characteristics. The hydrazine method is a combustion method and
has been investigated by different researchers including our
laboratories [6-7, 9, 11-17, 90-98]. Since the hydrazine method is a
low temperature technique which produced uniform particles in
submicron to few micron sizes that helped in achieving well dense
materials in our ferrites studies, the method may also be adopted in
the present investigations of gas sensing and catalytic activities, as
high surface area particles are desired. Therefore, the first aim of
the present investigations is to synthesize metal oxides through
hydrazine method to achieve particle of uniform particle size
distributions for gas sensing and catalytic studies. Since there is
fairly a good correlation between the gas sensing and
catalytic/photo-catalytic activities and electrical properties found in
the literature on ferrites, perovskites, SnO2, TiO2, and ZnO, we
considered exploring these aspects on these oxides and this is our
second aim. In order to study these aspects we have chosen simple
ethanol and moisture (humidity) sensing on the oxides through the measurement of electrical conductivity at different temperatures. Further, in order to study the photocatalytic activity of TiO$_2$ and ZnO we considered a model methylene blue degradation as well as photodestruction of NO$_x$ and propanol. To find out effect of dopants on the electrical characteristics and in turn on the gas sensing and photocatalytic activities, we have chosen additives such as lithium in gamma ferric oxide, \(\gamma\)-Fe$_2$O$_3$, K in CuFe$_3$O$_4$, strontium in LaCoO$_3$ and LaMnO$_3$ and nitrogen and iron in TiO$_2$ and nitrogen in ZnO.
1.5. Methodology

i) The synthesis of the oxide systems through mainly oxalate/hydroxide and hydrazine modified precursor routes.

ii) The characterization of the metal oxalate, hydroxide and hydrazinated oxalates/hydroxides through chemical, infrared, thermal (DSC/TG/DTA), to establish the plausible formula.

iii) X-ray diffraction of the thermal products of the precursors and phase identifications.

iv) Microstructural studies through scanning electron microscope (SEM)

v) Investigation of electrical conductivity of the oxides in air and in gas and moisture atmospheres as a function of temperatures.

vi) Examination of UV-Vis diffuse reflectance spectra, electron spin resonance, X-ray photoelectron spectra on TiO₂ and estimation of nitrogen in TiO₂ and ZnO

vii) Assessment of methylene blue degradation on TiO₂ and ZnO in the sunlight and NOx destruction on TiO₂ in UV-Visible region

viii) Deriving a correlation between the gas sensing and photocatalytic activities and electrical characteristics.