SUMMARY AND CONCLUSION

6.1 Summary

The contents of the thesis are divided into six chapters. Each chapter can be summarised as follows:

Chapter 1

Chapter 1 gives the basic introduction on the material science field and its development over the period. The advent of nanotechnology, its impact on the research field and eventually on the modern technological devices has also been discussed. The nanomaterials can be synthesised in the various forms such as nanoparticles, nanorods, nanowires, nanocubes and nanospheres. Properties vary with respect to the size and shape the nano-material is prepared with. Metal oxides form the major component of material research field. Over the years ZnO, TiO$_2$, Cr$_2$O$_3$, Mn$_2$O$_3$, Co$_3$O$_4$, NiO, CuO, SnO$_2$, In$_2$O$_3$, Fe$_2$O$_3$, Y$_2$O$_3$, Bi$_2$O$_3$, spinels and perovskites are some of the metal oxides that have been extensively studied. Doping these metal oxides with different metal ions also results in altering the properties of material which can add on to their applications in various fields. Different methods are available for synthesizing metal oxides in nanoform majorly forming two categories viz top down and bottom up approach. Few of the bottom up methods have been mentioned in this chapter. Dilute magnetic semiconductor (DMS) is an important field recently associated with metal oxides has been introduced. It has been shown that metal oxides when prepared in nanoform finds several applications in fields like catalysis, photocatalysis, biomedical appliances as well as in drug delivery agents. Further in this chapter the highlights of the thesis and organisation of the chapters is presented.

Chapter 2
Chapter 2 presents the literature survey on the metal oxides that are studied in this thesis and their related properties. First the introduction about the DMS material is presented. The DMS originated from the discovery of magnetism in transition metal doped II-VI semiconductors like CdTe, CdSe, ZnSe and CdS. A series of theoretical and experimental studies followed where transition metal doped metal oxides have come forward as the strong candidates in the DMS field. The highlighting report in this field was the observation of unusual ferromagnetism in the undoped diamagnetic oxides. Number of models and theories put forward to explain the observed ferromagnetism have been discussed in this chapter. Most of the theories relate the origin ferromagnetism to the lattice defects such as cation/anion vacancies or cation anion interstitials. Till today the topic has been controversial and findings are in progress to understand and substantiate the origin and existence of the ferromagnetism in such compounds.

Further this chapter deals with understanding the structure and properties of indium oxide and doped indium oxide material, where it is shown that the In$_2$O$_3$ crystallise in a cubic bixbyte structure. Different methods have been discussed for the synthesis of pristine and doped In$_2$O$_3$ nanoparticles and thin films including sol gel, combustion co-precipitation, hydrothermal/solvothermal, RF/magnetron sputtering, PLD and CVD.

The electrical properties studied for these materials have been discussed which displays the increase in electrical resistance on doping with transition metal. The magnetic properties observed are conflict-ridden where some report RT ferromagnetism in TM doped In$_2$O$_3$ nanoparticles whereas others observed paramagnetic behaviour. Various explanations are given to substantiate the observed results, where ferromagnetism is explained to be originating from the oxygen vacancies and in few cases from cation interstitials.
Indium oxide (In$_2$O$_3$) nanoparticles have been gaining importance in the catalytic field recently and several organic transformations that are carried out using this catalyst have also been discussed. This proves that In$_2$O$_3$ is highly applicative material and has a lot of potential in material chemistry and catalysis.

The literature on cerium oxide (CeO$_2$) describes that it crystallises in a face centered cubic fluorite structure with space group Fm$\overline{3}$m. The lattice when exist with oxygen vacancies, there is a presence of Ce$^{3+}$/Ce$^{4+}$ redox states. This property makes it an interesting material and can be exploited for several applications including catalysis. There are different methods reported in the literature for synthesizing CeO$_2$ in nano-size. The widely used methods are discussed in this chapter such as sol-gel, combustion, microwave assisted hydrothermal and co precipitation.

The literature also demonstrates the presence RT ferromagnetism in CeO$_2$. Transition and non-transition metal doped CeO$_2$ nanoparticles have been reported to display the dilute magnetism thus making it a strong candidate in DMS field. Presence of weak ferromagnetism in pristine compound has also been shown. It is well known that CeO$_2$ is used in different catalytic reactions. The organic reactions catalysed by CeO$_2$ are discussed here. It is widely used as the support material for CO oxidation reaction owing to the mobility of the oxygen species into the lattice.

Ferrites are cubic spinels with formula AB$_2$O$_4$. They crystallize in a face centered cubic structure with Fd$\overline{3}$m space group. The MgFe$_2$O$_4$ is one of the widely studied ferrite, when synthesized in a nanosize shows a super paramagnetic nature which finds application in magnetic resonance imaging, ferro-fluids, magneto-caloric refrigeration, drug delivery etc. It is a soft ferrite and there are several methods reported in the literature
for its synthesis in nano-range including combustion, sol gel, combination of both known as sol-gel combustion and co-precipitation.

Pristine and doped ferrite materials are a very important class of materials where the properties depend on the occupancy of cations in octahedral and tetrahedral sites. Many transition and rare earth doped MgFe$_2$O$_4$ compounds have been reported in the literature and their magnetic properties have been discussed. Ferrites have also entered the field of heterogeneous catalysis and the available reports are presented in this chapter.

**Chapter 3**

Chapter 3 describes experimental work including the methods of preparation of nanoparticles presented in this thesis and the instrumental techniques used to characterise them. Pristine and Co, Cr and Ag doped In$_2$O$_3$ nanoparticles have been synthesized by combustion method using glycine as a fuel. The voluminous compound was obtained on combustion for all dopants and their respective concentrations. It was then calcined and sintered at desired temperatures. Pristine and In doped CeO$_2$ and MgFe$_2$O$_4$ have synthesized by sol-gel method using citric acid. The mixture of metal nitrates and citric acid forms a gel on heating which further undergoes decomposition forming the compound. The obtained compound was then ground, calcined and sintered at desired temperatures.

The precursor gels obtained during the preparation were characterised by thermo gravimetric analysis where the decomposition process was monitored. The final compounds were then subjected to several characterisation techniques such as XRD, IR, UV-DRS, SEM, TEM, XPS and Mössbauer in case of ferrite compound. Two probe DC electrical resistivity and VSM were used for electrical and magnetic studies. The NMR
spectroscopy was used to characterise the reaction products catalysed by the nanoparticles. All the instrumentation techniques have been described in this chapter.

Chapter 4

All the spectroscopic and solid state analysis, their observations and results are discussed in this chapter.

The thermo-gravimetric (TG) analysis accompanied by DTA/DSC for $\text{In}_{1.88}\text{Co}_{0.12}\text{O}_3$, $\text{In}_{1.90}\text{Cr}_{0.10}\text{O}_3$ and $\text{In}_{1.96}\text{Ag}_{0.04}\text{O}_3$gel shows the initial weight loss owing to the loss of water molecule accompanied by endothermic peak followed by the major weight loss resulting from the combustion reaction which is accompanied by a sharp exothermic peak at 200°C. No major weight loss is observed beyond 230°C. On decomposition the metal oxides are formed and the organic impurity gets converted to oxides of carbon and nitrogen.$\text{Ce}_{0.90}\text{In}_{0.10}\text{O}_2$gel shows that initial weight loss is followed by decomposition that proceeds in two steps with distinct exothermic peaks at 207 and 294 °C. Compound is highly stable beyond 310 °C. For $\text{MgFe}_{1.96}\text{In}_{0.04}\text{O}_4$gel initially weight loss is due to loss of water followed by decomposition reaction which accompanied by two exotherms at 206 °C and 322 °C. The compound is found to be stable beyond 400 °C.

The X-ray powder pattern for pristine and Co, Cr and Ag doped $\text{In}_2\text{O}_3$ compounds show that they crystallize in a cubic bixbyte structure. No impurity phase is observed except for $\text{In}_{1.90}\text{Ag}_{0.10}\text{O}_3$composition which shows a secondary phase of silver oxide. All the peaks were matched with the JCPDS data and indexed with their corresponding $hkl$ values. The lattice parameters and crystallite size calculated by Sherrer’s formuladepict the nano-crystalline nature of the compounds. The XRD powder pattern for pristine and In doped $\text{CeO}_2$compounds shows that it crystallizes in a fluorite structure. The peaks are
matched with the JCPDS data and the corresponding $hkl$ values are indexed. The crystallite size reveals the nano-crystalline nature of all compounds. X-ray powder pattern for pristine and In doped MgFe$_2$O$_4$ depicts the cubic spinel structure. All the compositions form single phase except for MgFe$_{1.84}$In$_{0.16}$O$_4$, which shows an impurity peak corresponding to $\alpha$-Fe$_2$O$_3$. The crystallite size is obtained in nano range and lattice parameters have also been calculated.

The infrared spectra for gel as prepared and sintered sample are presented for all the compounds. The gel shows the presence of organic moiety and their corresponding vibrations coming from glycine in case of pristine and doped In$_2$O$_3$ and citric acid in case of pristine and CeO$_2$ and MgFe$_2$O$_4$ compounds. In the as prepared samples some of these peaks start disappearing and the peaks corresponding to metal oxides become visible. In the sintered samples no organic impurity is observed and the metal oxide peaks corresponding to In-O vibrations are observed at 601, 567 and 538 cm$^{-1}$ and for MgFe$_2$O$_4$ at 578 and 408 cm$^{-1}$ corresponding to tetrahedral and octahedral M-O stretching respectively.

The UV DRS studies showed the presence of charge transfer band for all the samples and the band gaps have been calculated from Taucs plot. All the samples show a band gap in the semiconductor range.

The microscopic analyses were carried out on scanning and transmission electron microscope. All the compounds show spherical morphology with few aggregates in case of ferrite samples owing to their magnetic nature. The Ce$_{1-x}$In$_x$O$_2$ compounds showed flakes like appearance in SEM. The TEM displayed the exact particle size of compounds which is in the nano-meter range for all the compounds. The doping reduced the particle size compared to pristine in all the compounds except for Ag doped samples which was
found to increase. The ED patterns displayed the concentric rings corresponding to diffraction pattern and are indexed with their $hkl$ values.

X-ray photoelectron spectroscopy was employed to identify the valence states of the metal ions. In Co, Cr and Ag doped In$_2$O$_3$ compounds the observed oxidation states of the elements are Co$^{2+}$, Cr$^{3+}$, Ag$^{1+}$ and In$^{3+}$. In case of indium doped CeO$_2$, In$^{3+}$ was identified whereas for cerium a mixed valence states of Ce$^{3+}$ and Ce$^{4+}$. Oxidation states of the elements in In doped MgFe$_2$O$_4$ were Mg$^{2+}$, Fe$^{3+}$, and In$^{3+}$. In all the compounds deconvulated spectra of oxygen showed two peaks corresponding to lattice oxygen and oxygen defects.

Mossbauer spectra showed the appearance of sextet for pristine compound and as the dopant concentration increased the intensity of sextet was reduced while the paramagnetic doublet became more prominent, this is owing to the super paramagnetic nature of the compounds.

Electrical resistivity studies carried on two probe resistivity setup revealed the semiconductor behaviour of all the samples the resistivity was found to decrease with increase in temperature.

Magnetic studies for the samples were carried out on VSM. The magnetisation v/s field (M-H) and magnetisation v/s temperature (M-T) were the measurements carried out. The Co, Cr, Ag doped compounds showed weak ferromagnetism at room temperature with lower dopant concentrations whereas the paramagnetic ordering was found to be prominent at 50 K. The pristine In$_2$O$_3$ displayed a weak ferromagnetism at all the temperatures. Similarly pristine CeO$_2$ also showed weak ferromagnetism which was found to enhance on doping with indium. When compared with the bulk sample, observed ferromagnetism was found to be razed. This suggests that the dilute magnetic behaviour
originates from the defects in the crystal formed during the preparation which are prominent in the nanoscale. The FC and ZFC curves also depict the DMS behaviour. Whereas in case of In doped ferrite sample the saturation magnetisation decreases but the super-paramagnetic behaviour is enhanced on doping where compounds show negligible coercivity at room temperature. At 50 K the magnetisation as well as coercivity was found to increase. The blocking temperature was found to be reduced to RT for the doped compound at the applied field of 250 Oe. The AC susceptibility studies also substantiate for the super paramagnetic nature of the compounds.

Chapter 5

The CO oxidation reaction was carried out on the prepared nanoparticles, where Co doped In_2O_3 showed the best catalytic activity; the 100% CO conversion was achieved at 130 °C for In_{1.88}Co_{0.12}O_3 composition. The surface area and the porosity measurements of the catalyst In_{1.5}Co_0.5O_3 reveals the increase in surface area doping which influence the catalytic property. Few organic transformation reactions were also carried out using these catalysts, MgFe_{1.80}In_{0.20}O_4 was found to be active for Henry reaction giving nitro-aldol product and for Quinazolinone synthesis. The experimental procedure and the schemes are presented in this chapter. The IR and NMR of the products obtained have also been discussed.

Pristine In_2O_3 and In_{1.96}Ag_{0.04}O_3 nanoparticles were tested for the Invitro α-amylase and α-glucosidase inhibition activity, which is an effective strategy for type-2 diabetes management. The In_{1.96}Ag_{0.04}O_3 nanoparticles showed the best activity for inhibition of both the enzymes at a very low concentration when compared with pristine compound as well as with the standard drugs.
The pristine In$_2$O$_3$, In$_{1.96}$Ag$_{0.04}$O$_3$ and In$_{1.88}$Co$_{0.12}$O$_3$ were further tested for their toxicity effects on zebra fish and human blood samples. The results obtained are discussed in this chapter. No measurable toxicity was observed for all the compounds.

6.2 Conclusions

In conclusion, Pristine and Co, Cr and Ag doped In$_2$O$_3$ nanoparticles have been successfully synthesized by combustion method using glycine as a fuel. Pristine and In doped CeO$_2$ and MgFe$_2$O$_4$ nanoparticles were prepared using sol-gel method using citric acid. The gel precursors were characterised by TG-DTA/DSC analysis and the stability of the compound with respect to temperature was found out. The X-ray diffraction analysis confirmed the phase formation of the compounds by matching with the JCPDS data. Pristine and doped In$_2$O$_3$ compound crystallises in a cubic bixbybyte structure whereas pristine and doped CeO$_2$ compounds crystallizes in a fluorite structure. The cubic spinel structure of ferrite was also confirmed. The infrared analysis showed that the final compounds do not contain any organic impurity at the same time the respective M-O vibrations were also found to be present. The UV DRS data showed the absorption bands of all compounds and the band gaps were calculated using Taucs plot which lie in the semiconductor range. The spherical morphology and nanosize is confirmed from SEM and TEM analysis. The XPS validates the elemental oxidation states which are as follows Co$^{2+}$,Cr$^{3+}$, Ag$^{1+}$ and In$^{3+}$ for In$_{1-x}$M$_x$O$_3$ (M=Co, Cr and Ag) compounds. Cerium showed a mixture of Ce$^{3+}$ and Ce$^{4+}$ along with In$^{3+}$ for Ce$_{1-x}$In$_x$O$_2$ compounds. The oxidation states of elements observed for MgFe$_{2-x}$In$_x$O$_4$ compounds are Mg$^{2+}$, In$^{3+}$ and Fe$^{3+}$. The oxygen showed two peaks corresponding to lattice oxygen and oxygen vacancies for all the compounds. The mössbauer data revealed the existence of super paramagnetic relaxation in the In doped MgFe$_2$O$_4$ compounds. The magnetic studies carried on pristine In$_2$O$_3$ and CeO$_2$ showed weak ferromagnetism at RT and 50 K. Co ,Cr and Ag doped samples also

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revealed weak ferromagnetism at RT, which is found to be razed as the concentration of dopant increased and also when measured at 50 K. The paramagnetic /anti-ferromagnetic ordering is found to be more favourable. The In doped samples showed enhancement in the magnetic property as the concentration of dopant increased at temperatures, 300 and 50 K. The super paramagnetic behaviour was observed at RT. When compared with bulk sample both In$_{1-x}$Co$_x$O$_3$ and Ce$_{1-x}$In$_x$O$_2$ showed decreased or absence of the magnetic behaviour observed in nanoscale. Thus we conclude that the Dilute magnetism observed in these compounds originate from the lattice defects such as oxygen vacancies or cation/anion interstitials, and are more prominent at nanoscale. Magnetic studies on indium doped MgFe$_2$O$_4$ nanoparticles revealed the super paramagnetic nature, where doping reduces the coercivity to almost zero and $T_c$ is lowered to room temperature T applied field of 250 Oe. The AC susceptibility study and mössbauer data also substantiates the super-paramagnetic nature of the nanoparticles. The CO oxidation studies showed the best CO conversion activity of Co doped In$_2$O$_3$ sample where 100% conversion was obtained at 130 °C for In$_{1.88}$Co$_{0.12}$O$_3$, which can be attributed to the smaller particle, size high surface area and porosity as well as the to the oxygen mobility of the compound. The MgFe$_{1.80}$In$_{0.20}$O$_4$ was found to be the best catalyst for organic transformations such as Henry reaction and quinazolinones synthesis at room temperatures. In$_{1.96}$Ag$_{0.04}$O$_3$ nanoparticles showed the enzyme inhibition activity towards $\alpha$-amylase and $\alpha$-glucosidase at a very low concentration of 100$\mu$g/mL and 0.18$\mu$g/mL respectively and hence displays its property as a starch blocker. The toxicity studies of pristine In$_2$O$_3$, In$_{1.96}$Ag$_{0.04}$O$_3$ and In$_{1.88}$Co$_{0.12}$O$_3$ on zebra fish embryos and human blood cells do not show distinct / measurable toxicity thus proving their application to be safe.