CHAPTER VI

Summary and scope for the future work

This chapter deals with the conclusions drawn on the basis of investigation of the various systems. Based on the results the future scope of the work is projected.

6.1 SPINEL

a) GAMMA FERRIC OXIDE (γ-Fe₂O₃)

i) From the various experimental work carried-out there is a correlation between the synthetic strategies, conductivity (ac and dc), sensing and catalytic activity.

ii) From the ac and dc conductivity studies it is clear that water plays an important role in the conduction mechanism of γ-Fe₂O₃ and lithium doped γ-Fe₂O₃. Lithium doped samples were found to be more moisture sensitive.

iii) The semi-conductivity in γ-Fe₂O₃ and lithium doped γ-Fe₂O₃ is due to the electrons, but the 3-4 order increase in the electrical conductivity observed in the lithium doped sample and significant increase in the conductivity in γ-Fe₂O₃ on exposure to moisture suggests that the conduction may involve the protons H⁺ (hydronium ion) and lithium ions. There may be some contribution of ionic and electronic conductivity in the system.
iv) The protonic conductivity in \( \gamma-\text{Fe}_2\text{O}_3 \) may be attributed to the hydrogen iron oxide phase as explained in DC conductivity studies [122], as it was observed that water plays a crucial role in stabilizing the phase.

v) Sensitivity studies carried-out on gamma ferric oxide and Lithiated \( \gamma-\text{Fe}_2\text{O}_3 \) show that lithiated samples are more sensitive than unlithiated \( \gamma-\text{Fe}_2\text{O}_3 \). Li doping enhances the conductivity, which may be due to the diffusion of \( \text{Li}^+ \). 1\% Li doped \( \gamma-\text{Fe}_2\text{O}_3 \) shows increased sensitivity for humidity.

vi) Ethanol sensitivity is enhanced with the increasing Li content, but undoped \( \gamma-\text{Fe}_2\text{O}_3 \) is a good LPG sensor. Experiments on sensing studies have shown that \( \gamma-\text{Fe}_2\text{O}_3 \) and lithiated \( \gamma-\text{Fe}_2\text{O}_3 \) can be effective humidity sensors.

vii) Catalytic studies have shown that NO\(_x\) reduction is better over Li-doped \( \gamma - \text{Fe}_2\text{O}_3 \) as compared to \( \alpha - \text{Fe}_2\text{O}_3 \). Alumina support favours the process. Hence we can infer that the superior catalytic activity of \( \gamma-\text{Fe}_2\text{O}_3 \) for NO\(_x\) reduction may be due to better semiconducting nature as compared to \( \alpha-\text{Fe}_2\text{O}_3 \), which has higher resistance. Thus, based on our experimental work there seems to be good correlation between the electrical conductivity (ac and dc), sensitivity studies and catalytic activity.

viii) To explore this correlation further it needs to study the electrical behaviour of these oxides under the various reaction conditions. Also there is need to investigate the response of electrical property to the NO\(_x\) and NH\(_3\) gases to understand the
mechanism of catalytic activity. Such work will be taken as a future scope of study in our laboratories.

b) Copper Ferrite and potassium substituted

Copper Ferrite \( \text{Cu}_1-x\text{K}_x\text{Fe}_2\text{O}_4 \) \((x = 0, 0.1)\)

i) The main objective in this system was to achieve single-phase copper ferrite , without a tenorite (CuO) as an impurity, at relatively lower temperature. The tetragonal phase of copper ferrite was found to be sensitive to catalysis [2], so substituting potassium in the copper ferrite stabilized it. \( \text{Cu}_{0.9}\text{K}_{0.1}\text{Fe}_2\text{O}_4 \) was synthesized by oxalate and oxalate hydrazinate method.

ii) Freeze-dried formate and oxalate precursors were tried for comparison as freeze-drying technique can conserve a highly disperse state of the various metal ions from aqueous solution, which decomposes at relatively lower temperature giving fine metal oxides.

iii) X-ray analysis of the thermal products of the freeze-dried samples shows formation of the tetragonal phase when the products were heated to \(~1000^\circ\text{C}\) and then slow cooling indicating the stabilization of the tetragonal phase.

iv) The saturation magnetization, \( M_s \), values of 21 and 28 emu/g were observed, respectively, for CuFe\(_2\)O\(_4\) and Cu\(_{0.9}\)K\(_{0.1}\)Fe\(_2\)O\(_4\), synthesized from oxalate precursor decomposed in controlled atmosphere of N\(_2\)/H\(_2\)O/air at 320\(^\circ\text{C}\). Also freeze dried oxalate and formate precursors of Cu\(_{0.9}\)K\(_{0.1}\)Fe\(_2\)O\(_4\) decomposed at 1000\(^\circ\text{C}\)
showed the saturation magnetization values of 30 and 38 emu/g.

v) Comparatively higher values of saturation magnetization may be attributed to the single-phase pure material that formed as shown by x-ray diffraction measurements. As our synthetic strategies using oxalate and hydrazinate precursors give CuFe$_2$O$_4$ and Cu$_{0.9}$K$_{0.1}$Fe$_2$O$_4$ in single phase without an impurity which can improve the catalytic activity, it can be taken up as future scope of study. Shangguan et al [3] have used CuFe$_2$O$_4$ and Cu$_{1-x}$K$_x$Fe$_2$O$_4$ ($x = 0.1, 0.2$) as catalyst for the simultaneous removal of NO$_x$ and diesel soot particulate.

c) Mn – Zn Ferrite (Mn$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$)

i) In Mn-Zn ferrite system we have obtained the single-phase spinel at low temperature with good saturation magnetization values. As the Mn-Zn ferrite is sensitive to the methods of preparation, sintering atmosphere, sintering temperature and sintering conditions play an important role in the formation of Mn-Zn Ferrite.

ii) According to different synthetic routes reported by various authors, as discussed in section 1.2.2 , high temperature sintering leads to loss of zinc and oxidation of Mn$^{2+}$ to higher oxidation states, if controlled atmosphere is not maintained. Thus, there are large variations in the magnetic measurements.

iii) In this context we have tried to synthesize Mn$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$ by oxalate precursor route followed by decomposition under
controlled atmosphere of N₂/H₂O/air at 320°C. The products of the decomposition were further heat treated in low oxygen partial pressure, p(O₂) = 10⁻⁵ atmosphere at 700°C and 900°C.

iii) X-ray diffraction pattern recorded for samples decomposed at 320°C under N₂/H₂O/air, and then further heating at 700°C and 900°C at oxygen partial pressure of 10⁻⁵ atmosphere showed the single-phase cubic spinel at lower temperature ~900°C. The saturation magnetization, Ms., values between 58-71 emu/g were recorded which otherwise required sintering temperature greater than 1200°C.

iv) As mentioned in the literature [13] Mn-Zn ferrite has been used as ceramic thick film humidity sensor. As in case of gamma ferric oxide and lithiated samples, semiconducting nature of Mn₀.₆₅Zn₀.₃₅Fe₂O₄, prepared by above method at lower temperature can be explored for sensing studies in future.

6.2 Perovskite

a) Lanthanum Aluminates /Sr substituted Lanthanum Aluminate (LaAlO₃ and a₀.₆₅Sr₀.₃₅AlO₂.₈₂₅)

i) Easy precursor technique using oxalate hydrazinate for the synthesis of LaAlO₃ and La₀.₆₅Sr₀.₃₅AlO₂.₈₂₅, produces powders at ~700°C. Ability of the products to form homogeneous microstructure is highly appreciable.

ii) X-ray diffraction patterns recorded at different higher temperatures for LaAlO₃ and La₀.₆₅Sr₀.₃₅AlO₂.₈₂₅ shows that cubic phase is obtained after sintering at 1000°C for LaAlO₃ and 1400°C for La₀.₆₅Sr₀.₃₅AlO₂.₈₂₅ with good sinterability.
iii) The dielectric loss (\(\tan \delta\)) is observed in all frequencies (1KHz-1MHz) studied for LaAlO\(_3\) beyond 300\(^\circ\)C, whereas La\(_{0.65}\)Sr\(_{0.35}\)AlO\(_{2.825}\) shows higher loss at much lower temperatures. From these observations it may be noted that the Sr doping increases the dielectric constant and dielectric loss of LaAlO\(_3\). However, the dielectric constant of 20 found in LaAlO\(_3\) is comparable to the reported \(\varepsilon'\) [20,79], while the value of 50 that observed in La\(_{0.65}\)Sr\(_{0.35}\)AlO\(_{2.825}\) is much higher than that obtained by solid-state reactions in the range of 1000-1550\(^\circ\)C. Samples can function as a good dielectric material in the wide frequency range, showing promising results even in the lower range of frequencies.

b) Sr-substituted lanthanum cobaltite (La\(_{0.8}\)Sr\(_{0.2}\)CoO\(_3\)\(-\delta\))

i) The main objective in this system was to obtain La\(_{0.8}\)Sr\(_{0.2}\)CoO\(_3\)\(-\delta\) with high ionic conductivity at relatively lower temperature. Synthesis was carried-out by oxalate hydrazinate method. La\(_{0.8}\)Sr\(_{0.2}\)Co(C\(_2\)O\(_4\))\(_3\).2N\(_2\)H\(_4\).3H\(_2\)O decomposed at lower temperature \(-700\)\(^\circ\)C, however the perovskite phase was formed \(-1000\)\(^\circ\)C as indicated x-ray diffraction pattern. It is also seen by endothermic peak in DSC curve \(-912\)\(^\circ\)C.

ii) X-ray diffraction measurement confirms the perovskite phase formation for La\(_{0.8}\)Sr\(_{0.2}\)CoO\(_3\)\(-\delta\) at 1000\(^\circ\)C however the poor perovskite phase formation is observed at 800 \(^\circ\)C.
c) Sr-substituted lanthanum manganite (La$_{0.7}$Sr$_{0.3}$MnO$_3$)

i) Our main objective in this system was to study the colossal magneto-resistance for La$_{0.7}$Sr$_{0.3}$MnO$_3$ synthesized by oxalate hydrazine method.

ii) Oxalate hydrazinate precursor La$_{0.7}$Sr$_{0.3}$Mn(C$_2$O$_4$)$_3$.2N$_2$H$_4$.15H$_2$O decomposes at relatively lower temperature $\sim$700°C, however the single phase perovskite may be formed at higher temperature.

iii) X-ray diffraction of the products sintered at 1000°C shows well crystalline nature of the material, however some impurity peaks are observed.

iv) Study of colossal magneto-resistance for La$_{0.7}$Sr$_{0.3}$MnO$_3$ synthesized by oxalate hydrazine method will be taken up as future scope of study. The preliminary results obtained will form the base for the future course of investigation.
6.3 Future scope of work

1. Electrical and magnetic and sensing studies need to be carried out on Mn-Zn ferrite prepared by oxalate and oxalate hydrazinate method.

2. Catalytic studies of CuFe$_2$O$_4$ and Cu$_{1-x}$K$_x$Fe$_2$O$_4$ (x = 0.1) for NO$_x$ and soot removal for samples obtained from oxalate hydrazinate method require to be carried out.

3. Synthesis, characterization and measurements of the colossal magneto - resistance (cmr) for La$_{0.7}$Sr$_{0.3}$MnO$_3$ prepared by oxalate hydrazine method.

4. Due to the good mixed ionic–electronic conductivity shown by La$_{0.8}$Sr$_{0.2}$CoO$_3$ synthesized by hydrazine method it is propose to study the synthesis, characterization and electrical properties of La$_{0.8}$Ba$_{0.2}$CoO$_3$ / Gd$_{0.8}$Sr$_{0.2}$CoO$_3$ / Gd$_{0.8}$Ba$_{0.2}$CoO$_3$ synthesized by oxalate hydrazine method.