Oxide spinels are a large class of compounds of mixed-metal oxides crystallizing into $\text{AB}_2\text{O}_4$ type structure. These systems are of immense technological importance due to their diverse applications in sensors, transducers, microelectronics, magnetoelectronic devices, telecommunication systems and industrially important catalytic and photocatalytic reactions. Spinel phase ferrospinels have been investigated in the past because of their potential applications in the field of electrical and magnetic devices. The surface acidity/basicity of some of the transition metal oxides is an important parameter to perform their activity in the field of catalysis. Spinel based gas sensor is an emerging trend to make them selective towards oxidizing and reducing gases. The surface electron donor properties of some of the mixed-metal oxides are also correlated with their acid-base behavior and catalytic activity. The interesting electrical and magnetic properties of these compounds are governed critically by their chemical composition. Hence preparation of oxide spinel, with specific properties has gained much importance. In recent years the synthesis of nanostructure materials plays a remarkable role in the field of material science. Their properties are much improved over the ordinary materials. They also show enhanced selectivity of catalyst, field of photocatalysis and as gas sensor.

Ferrospinels have a face centered cubic crystal structure with space group $\text{Fd}3\text{mO}^7_{h}$. The structure is derived from that of mineral spinel, $\text{MgAl}_2\text{O}_4$. Hence the unit cell formula is $\text{M}^{2+}_{8}\text{Fe}^{3+}_{16}\text{O}^{2-}_{32}$. The 32 oxygen ions form two kinds of interstitial sites- tetrahedral or A sites (four oxygen neighbors) and octahedral or B sites (six oxygen neighbors) per unit cell. In all, there are 64 tetrahedral and 32 octahedral sites.

By considering the opportunity in the field of material science, we have concentrate on the synthesis of ferrospinels, characterize them by various techniques and test out their catalytic, photocatalytic and gas sensing performance at elevated conditions. Therefore, the different ternary and quaternary systems were prepared by the substitution of divalent as well as trivalent transition metal ions at tetrahedral and octahedral sites. This thesis
describes the preparation, characterization and catalytic, photocatalytic and gas sensing evaluation of $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Mn}_x\text{O}_4$, $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Cr}_x\text{O}_4$ and $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$ spinel type oxide catalysts, photocatalyst and as gas sensors.

This chapter presents a brief summary of the work described in the preceding chapters; general conclusions arrived from the work. It contains the investigation of the following mixed-metal oxide systems with respect to structural, electrical, magnetic, spectral, dielectric properties with impedance study, gas sensing, photocatalytic and catalytic properties.

i) $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Mn}_x\text{O}_4$, $0.0 \leq x \leq 2.5$

ii) $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Cr}_x\text{O}_4$, $0.0 \leq x \leq 2.5$

iii) $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$, $0.0 \leq x \leq 1.0$

The compounds of the above mentioned systems were synthesized by new sol-gel method [1-7]. The A.R. Grade citric acid ($\text{C}_5\text{H}_8\text{O}_7\cdot6\text{H}_2\text{O}$) constituent metal nitrate were used as raw materials. The molar ratio of metal nitrate to citric acid was taken as 1:2. The metal nitrate was dissolved in a minimum amount of double distilled water to get a clear solution. The metal nitrate solution was mixed with citric acid solution to form metal-citrate complex. The mixed solution was heated at 100°C on a hot plate with continuous stirring. During evaporation, the solution became viscous and finally formed a very viscous gel. With further heating the viscous gel began frothing. After few minutes, the gel was automatically ignited and burnt with glowing flints. The auto-ignition was completed within a minute, yielding the black-colored ash termed as a precursor. The prepared powders of the sample were heated separately at elevated sintering temperatures.

The structural studies of the compounds were carried out by X-ray diffraction analysis. Some other physico-chemical properties viz. electrical, magnetic, spectral, thermal, structural, dielectric constant and impedance measurements were investigated. All the samples of the systems were investigated for their catalytic, photocatalytic and gas sensing activities.

Phase formation of all the samples were carried out by X-ray diffraction analysis using $\text{CuK}_\alpha/\text{CrK}_\alpha$ target. All the samples possess spinel-phase cubic
structure except Li$_{0.5}$Mn$_{2.5}$O$_4$ and Li$_{0.5}$Fe$_{0.5}$Mn$_{2.0}$O$_4$ possess tetragonal phase. The presence of cation over tetrahedral and octahedral site was studied from FT-IR. DC electrical resistivity measurements were carried out in the temperature range of RT to 623K. The plots of log $\rho$ vs. 1000/T were traced and the values of activation energy were calculated. SEM analysis was done to study the surface morphology of the samples. Nanostructure of the material was confirmed by Transmission Electron Microscopy. Compositional analysis was done by Electron Dispersive X-ray spectrophotometer equipped with SEM instrument. Study of thermal stability and the calculation of thermal kinetic parameters was done by TGA-DTA analysis. Various magnetic parameters like saturation magnetization, coercive field and remanent magnetization were measured by tracing hysteresis loop. Frequency dependent ac parameters and dielectric constant was measured at room temperature.

Catalytic performance of the catalyst was tested towards various oxime oxidation reactions. Photocatalytic performances were studied by different dyes solutions like methyl red, thymol blue and disperse red dyes in aqueous solution. Gas sensing activity was also performed towards various oxidizing and reducing gases/vapours at different operating temperatures.

The detail subject matter of the thesis is presented in seven chapters.

Chapter I deals with the introduction of oxidic spinels along with explanation and various applications in various fields. The high resistivity of these compounds is applicable in electronic devices while their interesting magnetic properties are used for the fabrication of various magnetic appliances. The structural, electrical, surface properties and thermal stability of the spinels also play a significant role in the field of catalysis, photocatalysis and gas sensors. The recent trend in nanotechnology is discussed in detail.

Chapter II contains the theoretical background of the various techniques such as XRD, SEM, TEM, FT-IR, DR-UV, XPS, TEM, TGA-DTA, TEP, magnetic hysteresis, dielectric and impedance study, gas sensing activity, photocatalytic activity and catalytic performance used in the investigation of the mixed-metal oxides.
Chapter III describes the details of experimental techniques used for the physico-chemical characterization of the spinels synthesized by sol-gel method.

Chapter IV deals with system Li$_{0.5}$Fe$_{2.5-x}$Mn$_x$O$_4$ ferrites. It is noted that, the manganese substituted lithium ferrites are cubic in the range $1.5 \leq x \leq 0.0$ and tetragonal in the range of $2.5 \leq x \leq 2.0$. The tetragonal structure for $x=2.0$ and 2.5 is due to the Jahn-Teller effect of Mn$^{3+}$ ions. The lattice constant increases with substitution of manganese content upto $x =1.5$, there after decreases due to the tetragonal distortion. The increase in lattice constant with increase in Mn content is due to the higher ionic radii of Mn$^{3+}$ (0.645Å) ions as compared to Fe$^{3+}$ (0.64Å) ions. Nonlinear trend in crystallite size, grain structure and magnetic behavior were observed with increasing Mn content. TEM analysis shows the nanostructure of the samples. The observed fringes in SAED pattern well match with X-ray pattern of the sample. In case of the Mn substituted lithium ferrite Fe concentration decreases means hopping conduction decreases conductivity decreases after addition Mn content. The compounds of Li$_{0.5}$Fe$_{2.5-x}$Mn$_x$O$_4$, samples $x = 0, 0.5, 1.0$ and 1.5 show N-type and $x =2.0$ and 2.5 show p-type conductivity. Magnetic study indicated that all the compounds are ferrimagnetic in nature. Dielectric property was studied by varying frequency and explained on the basis of electron-hole hopping mechanism. Impedance measurement analysis reveals a response that is dominated by a grain boundary behavior. The gas sensing study shows that lithium ferrite has selective response for LPG at 250°C. The photocatalytic degradation of methyl red indicates that lithium ferrite powders can effectively photodegrade methyl red under ultraviolet plus visible light irradiation. However, the photoactivity of all Mn-substituted ferrites powders was lower than the lithium ferrite.

Chapter V gives an account of the system Chromium-substituted nanocrystalline Zn-Mn ferrite. Samples were synthesized by sol-gel autocombustion method. X-ray diffraction studies confirm the cubic spinel structure formation of the samples. The lattice constant and crystallite size
Chapter VII: Summary and Conclusions

decrease with increase of Cr content. Thermal analysis confirms the, sintering temperature required for spinel phase formation. FTIR spectral studies indicate two absorption bands, one around 600 cm\(^{-1}\) (Tetrahedral) and the other weak around 500 cm\(^{-1}\) (Octahedral). Scanning Electron micrographs indicate the formation of uniform and fine grained samples. Transmission electron microscopy data reveal that the ferrospinels synthesized by auto-combustion method are in nanocrystalline range (~30-40nm). The content of the metals in the resulting spinel ferrites are close to the theoretical values as shown by EDAX measurements. The dielectric dispersion has been explained on the basis of electron-hole hopping mechanism. The dielectric loss decreases with increase in frequency and attains a constant value as the frequency increases. The ferrites show concentration dependence of ac electrical conductivity. Impedance measurements reveal that the impedance response is dominated by grain boundary behavior. The electrical resistivity is decreasing with increasing temperature for all the samples indicating that Cr-added ZnMnFeO\(_4\) ferrite have semiconductor-like behavior. Thermoelectric power measurement confirms all samples show P-type semiconducting nature. Various reducing and oxidizing gases were tested for gas sensing activity of all the compositions of ferrites. ZnMn\(_{0.25}\)Cr\(_{0.75}\)FeO\(_4\) shows remarkable response towards ethanol with good selectivity. The photocatalytic degradation of thymol blue dye indicates that ZnCrFeO\(_4\) powders can effectively photodegrade thymol blue under ultraviolet plus visible light irradiation. Oxidation of different oximes indicates that the ZnCrFeO\(_4\) is better catalyst with good selectivity.

Chapter VI includes the details of results and discussion of Li\(_{0.5}\)Fe\(_{2.5-x}\)Cr\(_x\)O\(_4\) system. X-ray analysis revealed that all the compositions are in cubic phase. The lattice constant ‘a’ goes on decreasing with increase in chromium content. Homogenous grain structure was observed from SEM while nanostructure was confirmed by TEM. SAED pattern of the samples also revealed the single-phase formation of spinel structure which agrees with XRD patterns. FT-IR study exhibited two prominent peaks in the region of 700 to 400 cm\(^{-1}\) which are due to tetrahedral and octahedral stretching
vibrations. Thermal stability as well as different kinetic parameters viz. entropy, activation energy, frequency factor were calculated from TGA-DTA analysis. Semiconducting behavior of the samples was investigated by the measurements of electrical resistivity. From the plots of log $\rho$ vs. 1000/T, the activation energy was determined. A linear decreasing trend in magnetic properties is observed from magnetic hysteresis loops of the samples. Dielectric study indicates the decrease in dielectric loss with the increase of frequency and attains a constant value as the frequency increases further. Impedance measurement analysis reveals a response that is dominated by a grain boundary behavior. The gas sensing study shows that, lithium ferrite has selective response for LPG at 250°C. The photocatalytic degradation of disperse red indicates that lithium ferrite powders can effectively photodegrade disperse red under ultraviolet plus visible light irradiation. However, the photoactivity of all Cr-substituted ferrites powders was lower than the lithium ferrite.

Chapter VII includes the summary and conclusion of the work carried out on the spinels. The results and analysis of the work can be summarized in following manner.

1. All the compositions of the studied systems show the formation of single-phase spinel cubic structure except $\text{Li}_{0.5}\text{Fe}_{0.5}\text{Mn}_{2.0}\text{O}_4$ and $\text{Li}_{0.5}\text{Mn}_{2.5}\text{O}_4$.
2. The appearance of two strong band in the range of 400 – 700 cm$^{-1}$ are due to tetrahedral and octahedral stretching vibrations.
3. Homogenous grain structure was revealed from SEM images and metal stoichiometry was confirmed by EDAX.
4. TEM analysis is in accordance with the x-ray results indicating that the particles are in nano-scale region.
5. From TGA-DTA analysis, the thermal stability and thermo-kinetic parameters were determined.
6. An electrical resistivity decreases with increasing temperature indicating semiconducting nature of all the samples.
7. To evaluate the nature of charge carriers, thermo-emf study was carried out.
8. All the samples showed hysteresis loop indicating ferrimagnetic behavior.
9. The dielectric behavior of the spinels is explained on the basis of polarization mechanism, which is similar to conduction mechanism.
10. The AC conductivity measurements are useful to understand the type of polarons responsible for the conduction.
11. Different compositions of the systems such as lithium ferrite and ZnMn$_{0.25}$Cr$_{0.75}$FeO$_4$ show remarkable gas response towards gases/vapours such as LPG and ethanol at various operating temperatures.
12. Catalytic and photocatalytic studies of all three systems were performed for different organic transformation reactions viz. oxidation of oxime and degradation different aqueous dyes like methyl red, thymol blue and disperse red. A good correlation between band gap, surface area and acidic sites with catalytic as well as photocatalytic performance was observed in all the systems.
References


