5.1 Introduction:

Mixed-metal oxide nanoparticles have been intensively studied in the last decade for their unusual physical and chemical properties owing to their extremely small size, large specific surface area and number of promising applications. Among various classes of nanomaterials, metal oxides are very common, most diverse and possess richest class in terms of physical, chemical and structural properties. The result and prospects of numerous applications of metal oxides, such as fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, dielectrics, lasers, magnets and catalysts have been discussed in literature [1-13].

Recently, considerable effort has been made on the preparation of surface modified nanoparticles of different types of metal oxides. Various methods are available for the synthesis of metal oxides, such as microwave refluxing [14], sol-gel [15-16], hydrothermal [17-18], co-precipitation [19-20], citrate-gel [21] and spray pyrolysis [22] etc. The selection of appropriate synthetic procedure often depends on the desired properties and final applications. Among these synthesis techniques, sol-gel autocombution method has several advantages over others for preparation of nanosized metal oxides as the process begins with a relatively homogeneous mixture and involves low temperature conditions and results a uniform ultrafine porous powders [23]. This method was employed by us to obtain improved powder characteristics, better homogeneity and narrow particle size distribution, thereby influencing structural, electrical and magnetic properties of spinel ferrites [24-26]. Spinel ferrites find potential applications in electrical components, memory devices, magnetostrictive and microwave devices over a wide range of frequencies because of their high resistivity and low losses [27-31]. The field of ferrites is well explored, due to their potential applications and the interesting physics involved in them.

In this topic, we report preparation of nanosized chromium substituted Zn-Mn ferrites by sol-gel autocombution method. It is a simple process, which offers a significant saving in time and energy consumption over the traditional
methods, and requires lower sintering temperature. This method was employed to obtain improved powder characteristics, more homogeneity and narrow particle size distribution, thereby influencing their structural, electrical and magnetical properties. The structural, electrical and magnetical properties were investigated by X-ray diffraction (XRD), TEM, SAED, Energy dispersive x-ray spectroscopy, DRS, FTIR spectroscopy, VSM study, Electrical conductivity and dielectric properties and the results have been discussed in details.

5.2. Materials and Methods:

5.2.1. Synthesis Technique:

Analytical grade chromium nitrate [Cr(NO$_3$)$_3$.9H$_2$O], iron nitrate [Fe(NO$_3$)$_3$.9H$_2$O], zinc nitrate [Zn(NO$_3$)$_2$.6H$_2$O], manganese nitrate [Mn(NO$_3$)$_2$.4H$_2$O] and citric acid [C$_6$H$_8$O$_7$.H$_2$O] were used to prepare ZnMn$_{1-x}$Cr$_x$FeO$_4$ (where x = 0.0, 0.25, 0.50, 0.75 and 1.0) by sol-gel method and Flow diagram for auto combustion technique is shown in Fig.5.1. Metal nitrates and citric acid were dissolved in minimum quantity of deionized water with 1:1 molar ratio. The pH of the solution was adjusted to about 9.0 to 9.5 using ammonia solution. The solution was transformed to dry gel on heating to 353K. On further heating the dried gel burnt in a self propagating combustion manner until all the gel completely converted to a floppy loose powder. The as burnt precursor powder was then sintered at 973, 1073 and 1173K for 8 h for confirmation of phase formation. The sintered powders were granulated using 2 % polyvinyl alcohol as a binder and uniaxially pressed at a pressure of 8 ton /cm$^2$ to form pellets. These pellets were gradually heated to about 773K to remove the binder material.

The phase formation of the sintered samples was confirmed by x-ray diffraction studies using a Philips PW-1710 x-ray diffractometer with CrK$\alpha$ radiation ($\lambda$=2.2897Å) or CuK$\alpha$ radiation ($\lambda$=1.54056Å) in a 0–20 geometry at standard atmospheric conditions. FTIR study was used to indicate the vibrational modes in the samples. The FTIR spectra were recorded using Perkin Elmer FTIR in KBr pellets. Infrared spectroscopic studies revealed two
main absorption bands in the range 400-800 cm\(^{-1}\) arising due to tetrahedral (A) and octahedral (B) stretching vibrations. The morphology and particle size analysis was carried out on a transmission electron microscope (TEM-Model Philips 200 CX) operated at an accelerating voltage of 300 KV. In all the studied compositions, spherical crystalline nanoparticles of about 30 nm size were observed by Transmission Electron Microscopy (TEM) technique. Formation of spherical nanoparticles was revealed by Scanning Electron Microscopy (SEM) analysis. The compositional analysis was performed by an energy dispersive x-ray system (EDAX). The elemental analysis as obtained from EDAX is in close agreement with the expected composition from the stiochiometry of reactant solutions used. Dielectric constant, dielectric loss tangent, ac conductivity and complex impedance were measured as a function of frequency in the range 20 Hz to 1 MHz. Frequency dependence of dielectric constant shows dielectric dispersion due to the Maxwell–Wagner type of interfacial polarization. The role of chromium in modifying structural and dielectric properties of these ferrites has been explained.
Fig. 5.1. Flow diagram for sol-gel autocombustion technique
5.2.2 Materials Characterization:

Thermal analysis of the different compositions of the Cr-substituted ZnMn ferrite system was carried out from the curves of TG-DTA. Stability of the dry citrate complexes was checked by scanning the thermograms in the temperature range of 10-1000°C in static air at the heating rate of 10⁰C/min. Different kinds of thermodynamic and kinetic parameters were determined from the plots of TG-DTA curves.

The phase formation of the samples calcined at different temperature was confirmed by X-ray diffraction studies using Philips PW-1710 X-ray diffractometer with CuKα radiation (λ=1.54056Å). The lattice parameters were calculated for the cubic and tetragonal phase using following relations.

\[ a = d \left( h^2 + k^2 + l^2 \right)^{1/2} \]  
\[
\text{where, } a \text{ and } c = \text{Lattice parameter, (hkl) = Miller indices}
\]
\[ d = \text{interplanar distance} \]

The crystallite size of sintered ferrites was calculated from the full width at half maxima of the most intense (311) peak by using Scherrer’s formula.

\[ t = \frac{0.9 \lambda}{\beta \cos \theta} \]  
\[
\text{Where, symbols have their usual meaning.}
\]

The X-ray density was calculated according to the formula

\[ \rho = \frac{8M}{Na^3} \]  
\[
\text{where, } N = \text{Avagadros number (6.023 X 10^{23} atom/mole)}
\]
\[ M = \text{Molecular weight, and} \]
\[ a = \text{lattice constant which was calculated from the X-ray diffraction pattern. X-ray density is sometimes also called ‘theoretical density’.} \]

Bulk density and apparent porosity of sintered specimens were determined by Archimedes principle. Sintered samples were weighted in dry state. Samples were immersed in water and kept under a vacuum of 4 mm of mercury for 5 hrs to ensure that water filled up the open pores completely. Then, soaked and suspended weights were measured. The apparent porosity and bulk density were calculated as follows: Dry weight of the sample = \( W_d \), Soaked weight of the sample = \( W_s \), Suspended weight of the sample \( W_a \).
The percentage porosity of sample was calculated and using the formula
\[
P(\%) = \left( \frac{d_x - d_a}{d_x} \right) \times 100
\]
Where, \(d_x\) = X-ray density, 
\(d_a\) = actual density

The FT-IR spectra were recorded in the range of 400 to 1000 cm\(^{-1}\) on instrument Perkin Elmer – IR spectrophotometer (model E-2829) in KBr pellets.

The SEM micrograph of the samples was obtained using scanning electron microscope (JEOL JSM 6360). The grain size of all the samples was calculated by Leir and Howard method.

Elemental analysis of several composition of the system was carried out by using electron dispersive X-ray spectroscopy equipped with SEM instrument.

Transmission electron microscope (Philips CM 20) was used to evaluate the nanostructure of the typical samples. To study the phase structure of the samples SAED pattern were also recorded.

Magnetic measurements of all the compositions were carried out by using a high field hysteresis loop tracer. The measurements were done at room temperature. Saturation magnetization (Ms), coercive field (Hc) and remanent magnetization (Mr) of the samples were studied from the hysteresis loops of respective curves.

Frequency dependent dielectric properties like, dielectric permittivity, dielectric loss tangent, ac conductivity and complex dielectric impedance measurements were studied in the range of 20Hz to 1 MHz. Room temperature a.c. conductivity, dielectric loss tangent and complex impedance have been determined as a function of frequency. The dielectric permittivity and ac conductivity is usually calculated from the measured complex impedance as an inductor and calculated using the equations,
\[
\varepsilon' = \frac{C_d}{\varepsilon_0 A}
\]
\[
\sigma_{ac} = \varepsilon'\varepsilon_0\omega\tan \delta
\]
where, C is capacitance of the pellet, d is thickness and A is cross sectional area of the flat surfaces of the pellet, ε₀ is dielectric permittivity and ω = 2nf is the angular frequency.

Two probe techniques was employed to measure the D.C. resistivity of the samples in the temperature range of room temperature to 723 K and specific resistivity was determined using the relation,

\[ \rho = \left( \frac{\pi d^2}{4t} \right) R \]  ---------5.8

The values of activation energy (eV) were calculated from the plots of log ρ Vs 10³/T. Silver paste was applied to both the surfaces of the pellets for good ohmic contacts.

The thermo-emf measurements were carried out in the temperature range of 300 K to 523 K. The graph of ΔV vs ΔT was plotted and the type of the conduction (n or p type) was evaluated.

Solvent free oxidation of oxime using tert-Butyl hydroperoxide as source medium was investigated by using 0.1g of ZnMn₁ₓCrₓFeO₄ (where x = 0.0, 0.25, 0.50, 0.75 and 1.0) ferrites. All compositions of the system were utilized for their catalytic activity towards oxidation of oxime. Various physico-chemical parameters like amount of catalyst, time span, solvent polarity effect was studied in detail. ZnMnFeO₄ was used as a model catalyst to optimize superior reaction conditions. In a typical experiment, 0.05 – 0.25 g of previously dried catalyst was taken in 25 mL two neck round bottom flask, then 5 mmol of oxime and 10 mmol of tert-Butyl hydroperoxide were added. The above reaction mixture was heated at 60°C in oil bath. The progress of the reaction was checked by thin layer chromatography. After completion of reaction, the catalyst was filtered off. The filtered catalyst was washed with hot ethanol and reused for next catalytic reaction. The oxime oxidation product was isolated by evaporating the solvent, purified by recrystallization, distillation and characterized by GC/MS. The reaction product was analyzed by Gas chromatography (NETEL India, Silica Capillary Column, FID, Column temperature as 120°C for 5 min. followed by heating rate 10°C/min up to 220°C, detector temperature 250°C).
Gas sensing performance of Cr-substituted Zn-Mn ferrite was tested against various oxidizing and reducing gases. The electrical resistance of a sensor in dry air is measured by Keithley Autoranging Picoammeter - Cleveland OH with use of conventional circuitry in which the sensor is connected to an external resistor at circuit voltage of 10 V (Aplab 7212 regulated power supplier). The values of device resistor are obtained by monitoring the output voltage across the load resistor. The resistance of the sensor was measured in the presence and absence of the test gas. A known amount of gas was introduced to attain the required level of its concentration. The gas sensing measurements were carried out at different operating temperatures (373 – 623 K). The gas response (S) is defined as the ratio of $\Delta R$, i.e. the change in resistance of the sensor in air ($R_a$) and in presence of gas ($R_g$), normalized to the value of sensor resistance in air.

$$\text{(%)} \ S = \left| \frac{R_a - R_g}{R_a} \right| \times 100$$

Photocatalytic performance studied by using hazardous dyes like Thymol blue. Thymol blue is a well known dye and is considered as a model of a series of commonly used dyes in the industry. The photocatalytic activity of the samples was studied for Thymol blue dye in presence of Ultra-violet light with different times of exposure.
5.3 Results and Discussion:

5.3.1 Phase formation:

5.3.1.1. Thermogravimetric analysis:

TG and DTA curves for the dried sample of ZnMnFeO$_4$ sample are presented in Figure 5.2. The temperature of decomposition, crystallization and phase transformation of the as-prepared powder was studied using TGA-DTA measurement for the typical composition ZnMnFeO$_4$ in the temperature range 20 to 700$^\circ$C at a heating rate of 10 $^\circ$C/min. It can be seen from the figure that a one to one correlation exists between these thermoanalytical curves indicating that the thermal effects are accompanied by weight loss. There are three major steps in the decomposition process dehydration, decomposition of the anhydrous precursor to acetonedicarboxylate complex and decomposition of acetonedicarboxylate complex to ferrite. There is one endothermic and two exothermic peaks observed for the citrate decomposition followed by ferrite formation. First step below 150$^\circ$C is ascribed to the vaporization of absorbed water. Second step is from 200 to 350$^\circ$C associated with the residual organic matter including citric acid. The third step above 600$^\circ$C is due to weight loss of as received ZnMnFeO$_4$ powder. It indicates that the unreacted metal nitrate is oxidized in this step.

For the determination of various kinetic parameters, Coat and Redfern (32) and Piloyan - Novicova (33) methods were employed. Coat and Redfern method:

This is typical integral method and equation used in this method is represented as,

$$ \int \frac{-dx}{(1-2)^{n}} = A \phi \int \exp(-E^*/RT)dt \quad \text{---------} \quad 5.10 $$
The LHS of above equation has two different solutions namely
\[ 1-(1-\alpha)^{1-n}/1-n \text{ for } n \neq 1 \]
\[ \text{and } -\log (1-\alpha) \text{ for } n = 1 \]
in both the cases RHS of equation (5.10) has the solution
\[ \frac{\Delta R T^2 (1-2RT) \exp (-E^*/RT)}{\Phi E^*} \]
Equations (4.13) and (4.14) are obtained after taking logarithms.

\[ \log \left( \frac{1-(1-\alpha)^{1-n}}{T^2 (1-n)} \right) = \log \left[ \frac{AR(1-2RT)}{\phi E^* E^*} \right] - \frac{E^*}{2.303RT} \]
for \( n \neq 1 \)

\[ \log \left( \frac{-\log(1-\alpha)}{T^2} \right) = \log \left[ \frac{AR(1-2RT)}{\phi E^* E^*} \right] - \frac{E^*}{2.303RT} \]
for \( n = 1 \)

* When \( n=1 \) describes a first order kinetic reaction.

In ordinary thermal decomposition reaction \( \log [AR (1-2RT)/\Phi E^* E^*] \) is practically constant and plots of

\[ \log \left( \frac{1-(1-\alpha)^{1-n}}{T^2 (1-n)} \right) \text{ vs } \frac{1}{T} \text{ for } n \neq 1 \]
\[ \text{and } \log \left( \frac{-\log(1-\alpha)}{T^2} \right) \text{ vs } \frac{1}{T} \text{ for } n = 1 \]
respectively, results in a straight line with a slope \( E^*/2.303 \text{ R} \) for the correctly chosen value of \( n \).

The application of equations 5.16 and 5.17 to the present spinels reveals that a better straight line results with equation 5.17 and hence the order of the reaction is unity over the whole series of decomposition.

The equations can be applied by a simple graphical technique since there is theoretical justification for order of reaction 0, \( \frac{1}{2} \), \( \frac{2}{3} \) and 1 in said state kinetics.

\[ \text{Fractional weight loss } \left[ \alpha = \frac{w_t-w_f}{w_0-w_f} \right] \]
and the corresponding $(1-\alpha)^n$ have been calculated from TGA curve at different temperature and summarized in Table 4.1. The value of slope and energy of activation were obtained from **Fig. 5.3 to 5.4** and the plots show linear trend and is calculated by the equation

$$E_a = 2.303 \times R \times \log zh / KT.$$  \hspace{1cm} \text{------- 5.19}

$$\text{Intercept} = 2.303 \times \log z$$

where, $T$ = peak temperature

$h$ = Planck constant

$k$ = Boltzman constant

$R$ = Molar gas constant i.e. 8.314 J/K

In the two step decomposition process the first stage activation energy ($E_a$) is 60.96 kJ mol$^{-1}$ for all the precursors and second stage activation energy is 133.66 kJ mol$^{-1}$. These values are listed in **Table 5.2**. There is a good agreement between the values of frequency factor ($\log z$) and Entropy ($\Delta S$) which are calculated by both the CR and PN methods. The negative values obtained for entropy of activation point out that both the reactions are slower than the normal (34).  

**Fig.5.2.** TGA-DTA Spectrum for ZnMnFeO$_4$
Table No. 5.1 Evaluation of kinetic parameters of ZnMnFeO$_4$

$W_0 = 5.7816$ mg

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temp. (°C)</th>
<th>Residual Weight (Wt) mg</th>
<th>$\frac{W_t - W_f}{W_0 - W_f}$</th>
<th>$\ln \left[ \frac{\alpha}{T^2} \right]$</th>
<th>$\ln \left[ \frac{g(\alpha)}{T^2} \right]$</th>
<th>1000/T (K$^{-1}$)</th>
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Chapter V: The System $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$

Fig. 5.3 Graph of $\ln \left( \frac{\alpha}{T^2} \right)$ Vs. $1000/T$ for $\text{ZnMnFeO}_4$

Fig. 5.4 Graph of $\ln \left( g \left( \frac{\alpha}{T^2} \right) \right)$ Vs. $1000/T$ for $\text{ZnMnFeO}_4$
Table No 5.2 Thermokinetic parameters of the ZnMnFeO₄ system

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Step</th>
<th>TGA Activation energy (E) kJ mol⁻¹</th>
<th>Frequency factor (log z)</th>
<th>Entropy (ΔS) kJ mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnMnFeO₄</td>
<td>Coat-Redfern</td>
<td>I</td>
<td>11.01</td>
<td>5.74</td>
<td>-133.39</td>
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<td></td>
<td></td>
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<td>Piloyan</td>
<td>I</td>
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<td>5.71</td>
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<td></td>
<td>Novicova</td>
<td>II</td>
<td>59.99</td>
<td>8.55</td>
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</table>

5.3.1.2 X-ray diffraction analysis:

X-ray powder diffraction pattern of ZnMnFeO₄ nanoparticles sintered at different sintering temperatures like 973, 1073 and 1173K, are shown in Fig. 5.5. X-ray diffraction data reveals that the manganese substituted Zinc ferrites are cubic at temperature 973K and tetragonal at higher sintering temperature. The tetragonal structure is due to the Jahn-Teller effect of Mn³⁺ ions [35]. On increasing the sintering temperature, the diffraction peaks become narrower and sharper, suggesting the increase in particle size and crystallinity of the samples. Also, the x-ray diffraction data shows that, the tetragonal phase is observed at sintering temperatures higher than 973K.
5.3.1.3 Scanning electron microscopy:

The particle surface morphology was studied using Scanning Electron Microscopy technique (JEOL-JSM 5360 Microscope). The microstructure of the samples depends on the sintering temperature. The scanning electron micrographs of sintered samples at different temperatures 973, 1073 and 1173K are shown in Fig.5.6. It can be seen that, the average grain size and crystallinity is increased significantly with increasing the sintering temperature and also the particle size becomes more uniform at higher sintering temperature. At the sintering temperature of 973K, substantial grain growth occurs in which the ferrite grains are cubic and well crystalline in nature.
5.3.1.4 Fourier transform Infra-red spectroscopy:

The FT-IR spectra of all compositions sintered at different temperatures are shown in Fig 5.7. Waldron et.al. [36] have reported two absorption bands in normal ferrites and both the absorption bands depend on the nature of octahedral M-O stretching vibration and nature of tetrahedral M-O stretching vibration. From the earlier study of the vibrational spectra of ferrites the band
around 600 cm\(^{-1}\) is attributed to the intrinsic vibrations of tetrahedral complexes and the band around 400 cm\(^{-1}\) to that of octahedral complexes. It is well known that the vibrational frequencies depend on the cation mass, cation-oxygen bonding force, distance and unit cell parameter. The FTIR spectra of all sintered compositions studied here, show sharp bands for the samples sintered at higher temperatures (>973K). These bands are mainly dependent on Fe-O distances. It is revealed that in normal spinel ferrites both the bands depend on the nature of octahedral cations and to a lesser extent on tetrahedral ones. It is also observed that the frequency of the absorption bands gradually increases with increase in the volume of unit cell.
Fig. 5.7. FT-IR spectra for ZnMnFeO$_4$ at different Sintering temperature
a) 973K, b) 1073K and c) 1173K
5.3.2. Characterization for the system ZnMn$_{1-x}$Cr$_x$FeO$_4$ ($x = 0.0, 0.25, 0.50, 0.75$ and $1.0$)

Fig. 5.8 Flow diagram for Characterization ZnMn$_{1-x}$Cr$_x$FeO$_4$
5.3.2.1 X-ray diffraction analysis:

The structure and phase purity of the products were confirmed by analyzing the X-ray diffraction patterns. Fig. 5.9 depicts the XRD patterns of the different ZnMn$_{1-x}$Cr$_x$FeO$_4$ compositions and all x-ray parameters are summarized in Table 5.3-5.7. All the observed reflections could be assigned to cubic spinel lattice indicating their single phase nature. Unit cell parameters were determined by indexing the diffraction peaks in the XRD patterns. The variation of unit cell parameter with chromium content is shown in Fig. 5.10. It is observed that the unit cell parameter gradually decreases with increasing Cr content in the composition obeying Vegard’s law. The slow linear decreasing trend in the lattice parameter is attributed to the replacement of Mn$^{3+}$ (0.65 Å) ions by Cr$^{3+}$ ions, a slightly smaller ion (0.62 Å), in the system [37]. From the X-ray diffraction peaks, average particle size was estimated by using Scherrer’s formula. The crystallite size decreases with increase in Cr content as shown in Fig. 5.11 and it is observed to vary in the range of 30-25nm. The slow decreasing trend of unit cell parameter due to incorporation of lighter Cr$^{3+}$ ion in place of Mn$^{3+}$ leads to a gradual decrease in the x-ray density with increase in chromium content (Fig. 5.12). The x-ray density (dx), lattice constant (a) and crystallite size (t) of the compositions are given in Table 5.8.
Fig. 5.9. X-ray data for the system ZnMn$_{1-x}$Cr$_x$FeO$_4$
Fig. 5.10. Lattice constant (nm) vs composition (x) for the system \( \text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4 \)

Fig. 5.11. Variation of crystallite size with x in \( \text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4 \) ferrites
Fig. 5.12. Variation of X-ray density with x in ZnMn$_{1-x}$Cr$_x$FeO$_4$ ferrites
### Table No. 5.3 Indexed X-ray diffract meter pattern of ZnMnFeO$_4$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Relative Intensity I ( % )</th>
<th>$\theta$</th>
<th>d (observed) ($\text{Å}$)</th>
<th>d (calculated) ($\text{Å}$)</th>
<th>hkl</th>
</tr>
</thead>
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<td>2.9466</td>
<td>220</td>
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<td>35.79</td>
<td>2.5068</td>
<td>2.5131</td>
<td>311</td>
</tr>
<tr>
<td>3</td>
<td>15.4</td>
<td>43.49</td>
<td>2.074</td>
<td>2.079</td>
<td>222</td>
</tr>
<tr>
<td>4</td>
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<td>45.43</td>
<td>1.9948</td>
<td>1.9997</td>
<td>400</td>
</tr>
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<td>31.0</td>
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<td>1.5999</td>
<td>1.6039</td>
<td>422</td>
</tr>
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<td>63.15</td>
<td>1.4710</td>
<td>1.4746</td>
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**Structure:** Cubic

**Lattice constant:** $a = 8.41 \text{Å}$
Table No. 5.4 Indexed X-ray diffraction pattern of ZnMn$_{0.75}$Cr$_{0.25}$FeO$_4$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Relative Intensity I ( % )</th>
<th>2θ</th>
<th>d (observed) (Å)</th>
<th>D (calculated) (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.3</td>
<td>30.34</td>
<td>2.9431</td>
<td>2.9504</td>
<td>220</td>
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<td>2</td>
<td>100</td>
<td>35.72</td>
<td>2.5116</td>
<td>2.5178</td>
<td>311</td>
</tr>
<tr>
<td>3</td>
<td>18.4</td>
<td>43.42</td>
<td>2.0824</td>
<td>2.0875</td>
<td>222</td>
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<td>12.9</td>
<td>45.37</td>
<td>1.9971</td>
<td>2.0020</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>7.2</td>
<td>54.08</td>
<td>1.6944</td>
<td>1.6986</td>
<td>331</td>
</tr>
<tr>
<td>6</td>
<td>15.3</td>
<td>57.45</td>
<td>1.6026</td>
<td>1.6066</td>
<td>422</td>
</tr>
<tr>
<td>7</td>
<td>20.1</td>
<td>62.38</td>
<td>1.4874</td>
<td>1.4911</td>
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Structure: Cubic

Lattice constant: \( a = 8.39 \, \text{Å} \)
**Table No. 5.5 Indexed X-ray diffraction pattern of ZnMn\(_{0.5}\)Cr\(_{0.5}\)FeO\(_4\)**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Relative Intensity I (%)</th>
<th>(\theta)</th>
<th>(d) (observed) (Å)</th>
<th>(D) (calculated) (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>4.7805</td>
<td>4.7924</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>33.9</td>
<td>30.35</td>
<td>2.9421</td>
<td>2.9494</td>
<td>311</td>
</tr>
<tr>
<td>3</td>
<td>100.0</td>
<td>35.79</td>
<td>2.5068</td>
<td>2.5131</td>
<td>222</td>
</tr>
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<td>4</td>
<td>30.2</td>
<td>43.58</td>
<td>2.0749</td>
<td>2.0800</td>
<td>400</td>
</tr>
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<td>5</td>
<td>12.4</td>
<td>45.33</td>
<td>1.9990</td>
<td>2.0039</td>
<td>331</td>
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<td>17.8</td>
<td>53.09</td>
<td>1.6933</td>
<td>1.6886</td>
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<td>24.2</td>
<td>57.58</td>
<td>1.5994</td>
<td>1.6034</td>
<td>333</td>
</tr>
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</table>

**Structure: Cubic**  
**Lattice constant: a = 8.36 Å**
Table No. 5.6 Indexed X-ray diffraction pattern of ZnMn$_{0.25}$Cr$_{0.75}$FeO$_4$

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Relative Intensity ( % )</th>
<th>2θ</th>
<th>d (observed) (Å)</th>
<th>D (calculated) (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>18.44</td>
<td>4.8075</td>
<td>4.8194</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>22.8</td>
<td>23.325</td>
<td>3.8105</td>
<td>3.8200</td>
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<td>3</td>
<td>100.0</td>
<td>33.10</td>
<td>2.7037</td>
<td>2.7105</td>
<td>222</td>
</tr>
<tr>
<td>4</td>
<td>76.8</td>
<td>35.560</td>
<td>2.5225</td>
<td>2.5288</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>18.0</td>
<td>38.32</td>
<td>2.3466</td>
<td>2.3525</td>
<td>331</td>
</tr>
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<td>6</td>
<td>35.2</td>
<td>55.36</td>
<td>1.6580</td>
<td>1.6622</td>
<td>422</td>
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<td>7</td>
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<td>57.01</td>
<td>1.6140</td>
<td>1.6181</td>
<td>333</td>
</tr>
</tbody>
</table>

Structure: Cubic  
Lattice constant: a = 8.33 Å
### Table No. 5.7 Indexed X-ray diffraction pattern of ZnCrFeO₄

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Relative Intensity</th>
<th>θ (°)</th>
<th>d (observed) (Å)</th>
<th>d (calculated) (Å)</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>18.63</td>
<td>4.7589</td>
<td>4.7707</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>15.4</td>
<td>23.165</td>
<td>3.8365</td>
<td>3.8460</td>
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</tr>
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<td>3</td>
<td>100</td>
<td>33.00</td>
<td>2.7121</td>
<td>2.7188</td>
<td>222</td>
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<td>2.4905</td>
<td>400</td>
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<tr>
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<td>18.7</td>
<td>38.28</td>
<td>2.3490</td>
<td>2.3548</td>
<td>331</td>
</tr>
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<td>43.915</td>
<td>2.060</td>
<td>2.0651</td>
<td>422</td>
</tr>
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<td>16.6</td>
<td>49.420</td>
<td>1.8427</td>
<td>1.8472</td>
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</tbody>
</table>

**Structure:** Cubic  
**Lattice constants:** $a = 8.31$
Table 5.8 Data on lattice parameter, crystallite size, x-ray density, physical density, Porosity of ZnMn$_{1-x}$Cr$_x$FeO$_4$ ferrite samples.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Lattice constant (a) nm</th>
<th>Crystallite size (t) nm</th>
<th>X-ray density(dx gm/cm$^3$)</th>
<th>Physical density(da gm/cm$^3$)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.841</td>
<td>30</td>
<td>4.85</td>
<td>4.95</td>
<td>4.89</td>
</tr>
<tr>
<td>0.25</td>
<td>0.839</td>
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<td>4.80</td>
<td>4.87</td>
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<tr>
<td>0.50</td>
<td>0.836</td>
<td>28</td>
<td>4.78</td>
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</tr>
<tr>
<td>0.75</td>
<td>0.833</td>
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<td>4.82</td>
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</tr>
<tr>
<td>1.0</td>
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<td>25</td>
<td>4.75</td>
<td>4.78</td>
<td>6.23</td>
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</tbody>
</table>

5.3.2.2 Fourier Transform Infra-red spectroscopy:

The Infra-red spectra of the samples are shown in Fig. 5.13. It can be seen that the two spectral bands are less broadened for higher chromium content. Such broadening can be attributed to the statistical distribution of Fe at A-(tetrahedral) and B-(octahedral) sites. Waldron [36] ascribed the $\nu_1$ band to the intrinsic vibration of the tetrahedral group (~ 600 cm$^{-1}$) and $\nu_2$ to octahedral group (~ 475 cm$^{-1}$). The vibrational frequencies depend on cation mass, cation – oxygen distance and the bonding force. The values of the vibrational frequency for tetrahedral sites ($\nu_1$), octahedral sites ($\nu_2$) and differences ($\nu_1 - \nu_2$) are given the Table 5.9.

For un-substituted composition, viz. ZnMnFeO$_4$, the two bands observed at 595 and 455 cm$^{-1}$ are assigned to the $\nu_2$ and $\nu_1$ respectively. A comparison of the observed vibrational frequencies of all the studied compositions, indicates that the $\nu_1$ (corresponding to tetrahedral unit) remain almost unmodified with increasing Cr$^{3+}$ content. However, $\nu_2$ (corresponding to octahedral unit) increases smoothly with increase in Cr$^{3+}$ content e.g. 455 cm$^{-1}$ (for x = 0.0) to 487 cm$^{-1}$ (for x = 1.0). The increasing vibrational frequency ($\nu_2$) with increase in Cr$^{3+}$, can be attributed to the increasing force constant due to the shortening of M-O bonds in the octahedral unit. Thus, it seems that Cr$^{3+}$ preferably enters
to the octahedral site and hence affecting the force constant and bond lengths, without bringing about any change in tetrahedral site.

The difference between $v_1$ and $v_2$ (as $v_1 - v_2$) decreases with increasing Cr$^{3+}$ substitution. The decreasing values of ($v_1 - v_2$) indicate increasing separation between a- and d- sites [38]. Such an increasing separation of a- and d sites may weaken the a-d super exchange interaction. According to the theory, the variation of the super-exchange interaction affects significantly the magnetic behavior.
Table 5.9. Positions of IR absorption bonds and difference frequency values for ZnMn$_{1-x}$Cr$_x$FeO$_4$ ferrites system

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>$\nu_1$ cm$^{-1}$</th>
<th>$\nu_2$ cm$^{-1}$</th>
<th>$\nu_1 - \nu_2$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>595</td>
<td>455</td>
<td>140</td>
</tr>
<tr>
<td>0.25</td>
<td>591</td>
<td>463</td>
<td>128</td>
</tr>
<tr>
<td>0.50</td>
<td>588</td>
<td>475</td>
<td>113</td>
</tr>
<tr>
<td>0.75</td>
<td>595</td>
<td>483</td>
<td>112</td>
</tr>
<tr>
<td>1.0</td>
<td>594</td>
<td>487</td>
<td>107</td>
</tr>
</tbody>
</table>
5.3.2.3 Diffuse reflectance spectroscopy:

The UV–vis diffuse reflectance spectra of incorporated Cr substituted Zn-Mn ferrites are presented in Fig.5.14. With increasing the Chromium concentration, the band gap increases and a consequence the photocatalytic activities also increases. Furthermore, with the increase of the amount of Cr in ZnMn ferrite, the reflectance in the visible range of 400–700 nm decreases dramatically. This result proves that, upon addition of Cr substitution ZnMn ferrite particles, the absorption of the powders in the visible spectrum range increases significantly compared to that of the pure ZnMnFeO$_4$. This means
that the composite powders are sensitive to visible light. The obvious large red shift of the ZnCrFeO$_4$ powders is considered to be due to two factors. One of these comes from the mixing effect of band gaps and the other factor is considered to be the interface effect.

![DRS spectra for ZnMn$_{1-x}$Cr$_x$FeO$_4$](image)

**Fig.5.14** DRS spectra for ZnMn$_{1-x}$Cr$_x$FeO$_4$

$x = 0.0, 0.25, 0.50, 0.75 \text{ and } 1.0$
5.3.2.4. Scanning Electron Microscopy:

The SEM images of chromium substituted Zn-Mn ferrites are shown in the Fig. 5.15 (a-d). It is observed that the average grain size goes on decreasing with substitution of Cr content. The average grain size is smaller than 0.1µm for all the compositions. It can be seen that the grain size and crystallinity decrease significantly with increasing chromium content since the ionic radius of chromium is smaller than the ionic radius of manganese. The particle size becomes more uniform at higher chromium concentration.

Fig. 5.15. SEM micrographs for the system ZnMn$_{1-x}$Cr$_x$FeO$_4$

a) x =0.0, b) x = 0.25, c) x = 0.75 and d) x = 1.0
5.3.2.5. Transmission electron microscopy:

Figure 5.16(a-c) depicts transmission electron micrographs (TEM) of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system, where $x = 0.0$, $0.5$ and $1.0$, respectively. The corresponding selected area electron diffractograms (SAED) are given as inset in Figure 2a, 2b and 2c. It is evident from these micrographs that all the synthesized samples have spherical particles ranging from 30 to 40 nm. The superimposition of the bright spot with Debye ring pattern indicates crystalline nature of the samples. Both the figures confirm that most of the particles are of size about 30 nm. This is in close agreement with the average crystallite size obtained from XRD (Table-5.8)
5.3.2.6 Energy dispersion x-ray spectroscopy:

The composition of the nanocrystalline metal oxides has been determined using the energy dispersion x-ray analysis (EDAX). The X-ray spectra for \( x = 0.0, 0.5 \) and 1.0, compositions are shown in Fig.5.17 (a-c). From the EDAX spectra, the presence of Zn, Mn, Fe, Cr and O is confirmed in the sample. The quantitative analysis of EDAX spectrum revealed the relative atomic ratio of Zn: Mn: Fe of about 1:1:1, which is close to the expected values for ZnMnFeO\(_4\). The data of the EDAX analysis for all three samples are given in Table-5.10 and it is revealed that, the experimental value of the atomic percentage is in well agreement with assumed stoichiometry in preparation.
Chapter V: The System ZnMn_{1-x}Cr_xFeO_4

![Graph showing ZnMn_{1-x}Cr_xFeO_4 with x = 0.0](image)

![Graph showing ZnMn_{1-x}Cr_xFeO_4 with x = 0.5](image)
**Fig. 5.17.** EDAX data for the system ZnMn$_{1-x}$Cr$_x$FeO$_4$

$x = 0.0, 0.5$ and $1.0$

**Table 5.10.** Atomic percentage value for the ZnMn$_{1-x}$Cr$_x$FeO$_4$ system by EDAX analysis
5.3.2.7. Magnetic measurement:

Magnetic measurements of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system were carried out by using vibrating sample magnetometer (VSM) and they are depicted in Fig. 5.18. The samples show typical S-type shape in M–H curve, though the coercive fields are very small. The magnetization rises very sharply as the applied field increases from zero in either direction and then slowly approaches saturation. This is the typical behavior of nanosized magnetic material where residual superparamagnetic relaxation leads to slow rise in the wings and ferrimagnetic part contributes to hysteresis loop with small coercive field. In zinc ferrite the magnetization appears due to cationic inversion at smaller particle size. Thus as the particle size increases, the inversion decreases and the magnetization decreases. The magnetic data for the samples reveals that, it is ferrimagnetic in nature. The magnetic parameters such as saturation magnetization ($M_s$), remanant magnetization ($M_r$), and coercive field are summarized in Table 5.11.
Chapter V: The System ZnMn$_{1-x}$Cr$_x$FeO$_4$

\[ x = 0.25 \]

\[ M(\text{emu/gm}) \]

\[ H_c(\text{Oe}) \]

\[ x = 0.5 \]
Chapter V: The System ZnMn$_{1-x}$Cr$_x$FeO$_4$

Fig. 5. Hysteresis loops of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system.

$\mathbf{x = 0.75}$

$\mathbf{x = 1.0}$

$x = 0.0, 0.25, 0.50, 0.75 \& 1.0$
Table 5.11. Magnetic parameters of $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$ system

$x = 0.0, 0.25, 0.50, 0.75 \& 1.0$

<table>
<thead>
<tr>
<th>Composition $x$</th>
<th>Saturation magnetization</th>
<th>Remanant magnetization</th>
<th>Coercive field</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.0$</td>
<td>2.41 emu/g</td>
<td>1.79 emu/g</td>
<td>7.11 Emu/g</td>
</tr>
<tr>
<td>$0.25$</td>
<td>1.43 emu/g</td>
<td>1.60 emu/g</td>
<td>5.14 Emu/g</td>
</tr>
<tr>
<td>$0.50$</td>
<td>0.76 emu/g</td>
<td>1.10 emu/g</td>
<td>3.67 Emu/g</td>
</tr>
<tr>
<td>$0.75$</td>
<td>0.56 emu/g</td>
<td>0.89 emu/g</td>
<td>2.35 Emu/g</td>
</tr>
<tr>
<td>$1.0$</td>
<td>0.43 emu/g</td>
<td>0.77 emu/g</td>
<td>1.44 Emu/g</td>
</tr>
</tbody>
</table>

5.3. 2.8. Dielectric study:

5.3.2. 8.1. Dielectric constant ($\varepsilon'$) at room temperature with frequency:

Fig. 5.19 shows the variation of relative dielectric constant ($\varepsilon'$) with frequency. It is found that the relative dielectric constant increases steeply at lower frequencies and remains constant at higher frequencies, indicating the normal dielectric behavior. This dispersion behavior is attributed to the Maxwell-Wagner type interfacial polarization in accordance with Koop’s phenomenological theory [39-41]. According to this theory, the conductivity of grain boundaries contributes more to the dielectric constant at lower frequencies. In this model, the dielectric structure is assumed to consist of well-conducting grains which are separated by poorly conducting grain boundaries.

Iwauachi [42] and Rabinkin and Novikova [43] have pointed out that there is a strong correlation between the conduction mechanism (hopping) and
the dielectric behavior of ferrites. By electronic exchange, \( \text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+} \) and \( \text{Mn}^{2+} \leftrightarrow \text{Mn}^{3+} \), one obtains local displacement of the electrons in the direction of applied electrical field. These displacements determine the polarization of the ferrites. In the present case, it is observed that the dielectric constant goes on decreasing with the increase of \( \text{Cr}^{3+} \) concentration in ZnMn\(_{1-x}\)Cr\(_x\)FeO\(_4\) compositions. This is due to increase of resistivity of Zn-Mn ferrite with the substitution of \( \text{Cr}^{3+} \) concentration, as the dielectric behaviour is directly proportional to the square root of conductivity. A close examination of the figures indicates that the dispersion of \( \varepsilon' \) with frequency is maximum in the case of ZnMnFeO\(_4\) and it decreases on substitution of non magnetic chromium ions. A similar variation of the dielectric constant with frequency was observed for Mn and Cr substituted Li- ferrite [25-26].

The decrease in the polarization with increasing frequency is due to the fact that beyond a certain frequency of the electric field, the electronic exchange between ferrous and ferric ions cannot follow the alternating field. Such a variation of dielectric constant with frequency has been observed by Ravinder et.al [44].
Fig. 5.19. Variation of dielectric constant with frequency for ZnMn$_{1-x}$Cr$_x$FeO$_4$
System $x = 0.0, 0.25, 0.50, 0.75$ & $1.0$

5.3.2.8.3. Dielectric loss (tan $\delta$) at room temperature with frequency:

The variation of dielectric loss tangent (tan $\delta$) with frequency is shown in Fig. 5.20. The loss tangent decreases continuously with increasing frequency and attains a constant value at higher frequencies. At higher frequencies, losses are found to be low since domain wall motion is inhibited and magnetization is forced to change by rotation. The dispersion in tan $\delta$ is seen in the lower frequency region. A maximum value in tan $\delta$ can be observed only when the hopping frequency is equal to that of the externally applied electric field. The dielectric loss tangent decreases inversely with the frequency. Similar results have been reported by Kumar et.al [45] in Li-Ti ferrites and Ahmed et.al. [46] in Ni ferrites.
5.3.2.8.4. AC conductivity ($\sigma_{\text{AC}}$) at room temperature with frequency:

The variation of electrical conductivity of nanophase Cr-substituted Zn-Mn ferrites was calculated at different frequencies and is shown in Fig.5.21. It is observed that the ac conductivity increases with the increase in applied frequency for all the samples. The conductivity is dependent on the concentration of manganese ions. The ac conductivity has been related to the hopping of electrons between Fe$^{2+}$ and Fe$^{3+}$ [47-48] and the hopping rate increases with the increase in applied frequency. The substitution of Cr$^{3+}$ on B-site reduces the Fe$^{2+}$ concentration due to electron exchange.

$$\text{Cr}^{3+} + \text{Fe}^{2+} \leftrightarrow \text{Cr}^{2+} + \text{Fe}^{3+}$$
As stated earlier, the electron hopping energy between $\text{Cr}^{3+} \leftrightarrow \text{Cr}^{2+}$ is larger than that between $\text{Fe}^{3+} \leftrightarrow \text{Fe}^{2+}$. By increasing replacement of Mn by Cr ions, the number of ferrous ions at B-sites is decreased. As the concentration of Fe$^{2+}$ ions at B-sites is reduced, the electron exchange is suppressed. Hence, the ac electrical conductivity decreases with the increase in Cr content. Similar type of electron conduction mechanism in terms of electron and polaron hopping has been discussed earlier by Austin and Mott [49].

![Graph showing variation of ac conductivity with log $\omega^2$ for ZnMn$_{1-x}$Cr$_x$FeO$_4$ system](image-url)

**Fig.5.21.** Variation of ac conductivity with log $\omega^2$ for ZnMn$_{1-x}$Cr$_x$FeO$_4$ system
5.3.2.9. Complex impedance at room temperature with frequency:

The bulk and grain boundary contribution to the total conductivity can be separated out by using impedance measurements. The impedance spectrum is usually represented as real component of impedance ($Z'$) vs imaginary component of impedance ($Z''$). It is referred as Nyquist plot.

Typical impedance spectra for the present samples are shown in Fig. 5.22. A well resolved semicircle is observed for each sample between the frequency range 20 Hz to 1 MHz. The size of semicircle changes with grain size. The semicircles at higher and lower frequencies represent bulk and electrode process respectively, while that at intermediate frequencies represents grain boundary contribution [50]. The diameter of semicircle corresponds to the resistance of the grain [51].

![Nyquist plots for ZnMn$_{1-x}$Cr$_x$FeO$_4$ samples.](image)

**Fig. 5.22.** Nyquist plots for ZnMn$_{1-x}$Cr$_x$FeO$_4$ samples.
5.3.2.10 Electrical resistivity:

Temperature dependence of resistivity ($\rho$) of samples sintered at 973K for 8h were studied over the temperature range from room temperature to 623K and they are shown in Fig.5.23. It can be seen that the resistivity decreases with increasing temperature for all samples. The observed behavior clearly indicates that the present Cr-substituted Zn-Mn ferrites have semiconductor-like behavior. The change in resistivity is due to the presence of Fe$^{2+}$ ions. The resistivity arises due to the mobility of the extra electron, which comes from Fe$^{2+}$ through the crystal lattice. The movement is described by a hopping mechanism, in which the charge carriers jump from one ionic site to the next [52]. The decrease of the electrical resistivity with increasing temperature may be related to the increase of the drift mobility of thermally activated charge carriers (electron and hole) according to hopping conduction mechanism. In case of Cr-substituted Zn-Mn ferrites, Fe$^{2+}$ ion concentration decreases due to replacement by Cr$^{3+}$ion and decreases the hopping conduction. This results the increased resistivity in Cr-substituted Zn-Mn ferrites. The values of activation energy ($\Delta E$) varied between 0.39 and 0.60 eV which are summarized in Table 4.13.
Table No. 5.12 Average grain size from SEM and energy of activation from resistivity of the samples.

<table>
<thead>
<tr>
<th>Composition (x)</th>
<th>Average grain Size (µm)</th>
<th>Activation Energy, ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.33</td>
<td>0.39</td>
</tr>
<tr>
<td>0.25</td>
<td>0.31</td>
<td>0.44</td>
</tr>
<tr>
<td>0.50</td>
<td>0.29</td>
<td>0.50</td>
</tr>
<tr>
<td>0.75</td>
<td>0.27</td>
<td>0.59</td>
</tr>
<tr>
<td>1.0</td>
<td>0.25</td>
<td>0.60</td>
</tr>
</tbody>
</table>

Fig. 5.23. Electrical conductivity study of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system
5.3.2.11. Thermoelectric power measurement

The composition variation of seebeck coefficient as a function of temperature is shown in Fig.5.24. The samples ZnMn$_{1-x}$Cr$_x$FeO$_4$, where x = 0, 0.25, 0.50, 0.75 and 1.0 show p-type conductivity. The conduction mechanism in p-type specimens is predominantly due to hole transfer from Mn$^{4+}$ to Mn$^{3+}$ ions. The appearance of ‘p’ type carriers in the present case is due to hole transfer in Mn$^{4+}$ to Mn$^{3+}$.

Fig.5.24 Thermoelectric power measurement study of ZnMn$_{1-x}$Cr$_x$FeO$_4$ system
5.3.3 Applications

5.3.3.1 Gas sensing studies

Different mixed metal oxides such as NiFe$_2$O$_4$, CdFe$_2$O$_4$, ZnFe$_2$O$_4$ and CuFe$_2$O$_4$ have been studied for various gas-sensing applications. These oxides have been reported as both n and p-type semiconducting material. Development of gas sensors to monitor combustible gases is essential due to the concern for safety requirements in homes and for industries, particularly for the detection of LPG, which is one of the extensively used but potentially hazardous gases.

The sensitivity towards reducing gases is reported in n-type while for oxidizing gases like chlorine is reported in the p-type ferrite [53-58]. The gas sensing is a surface phenomenon of gas–solid interaction, where the conductivity of semiconducting oxides can be altered by adsorption of gases from ambient. It is well known that depending upon the morphology and operating temperatures, the oxide surface holds various oxygen species, such as O$^-$, O$^{2-}$, O$_2^-$. Their number and distribution also plays an important role in the gas sensing characteristics. The literature shows that the metal oxide nanoparticles enhance the sensitivity of a gas sensing material, while the selectivity is achieved by doping on surface or in the volume. However, recently Korotcenkov [59] suggested that the shape control of the nanocrystallites can provide energetically different adsorption sites for the test gases on different crystal facets. Thus existence of large surface to volume ratio in the typical nanostructured material facilitates better response towards specific gases. Moreover, morphology and particle size of nanomaterials depend upon their method of preparation and sintering temperature, and hence one can observe different responses towards gases for the similar composition.

In view of the possibility of finding gas response in the nanostructured ferrites ZnMn$_{1-x}$Cr$_x$FeO$_4$ system has been explored as a gas sensing material. It has been synthesized by a simple sol-gel route which plays a vital role in inhibiting the grain growth. The gas-sensing characteristics were recorded with reference to time at different operating temperatures and gas concentrations.
Chapter V: The System ZnMn$_{1-x}$Cr$_x$FeO$_4$

The change in electrical resistance was used as a measure of gas response at various temperatures.

Gas sensing performance of each composition of the ZnMn$_{1-x}$Cr$_x$FeO$_4$ system has been tested for various oxidizing and reducing gases viz. ethanol, LPG, H$_2$, Cl$_2$ CO$_2$ and ammonia gas. To investigate gas-sensing properties, the crystalline nanosized ZnMn$_{1-x}$Cr$_x$FeO$_4$ powder in the form of pellets was used. The pellets of diameter 8 mm and thickness 2 mm were made under pressure of 5 tons/cm$^2$ using hydraulic press followed by sintering at 400 $^\circ$C for 2 h. These pellets were then subjected for studying their sensitivity and selectivity at different controlled temperatures towards various gases in the dynamic setup. The response towards individual gas at elevated temperature is plotted in fig. 5.25.

It is seen from the figure that effect of Chromium substitution plays a significant role in the detection of various gases at different operating temperatures. It is notable that, ZnMn$_{0.25}$Cr$_{0.75}$FeO$_4$ shows remarkable response towards ethanol. Figure 5.26 shows response (%S) towards ethanol at various operating temperatures which indicates 250$^\circ$C as the optimum temperature for the gas response. Figure 5.27 shows the response of the material increased with increase in ethanol gas concentration. This indicates that, the sensor has large range of detection. Ethanol sensing mechanism also works in the same way, oxygen is adsorbed on the surface of the sensor from the air and then is transformed into chemisorbed oxygen at a definite temperature. The mechanism is represented in equation 5.20 – 5.22. The chemisorptions of ethanol vapors can be represented as,

$$\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \longleftrightarrow \text{C}_2\text{H}_5\text{OH} \text{(ads)} \quad \text{------- 5.20} \\
\text{C}_2\text{H}_5\text{OH} \text{(ads)} + \text{O}^- \text{(ads)} & \longleftrightarrow \text{C}_2\text{H}_5\text{O}^- \text{(ads)} + \text{H}_2\text{O} \text{(g)} \quad \text{------- 5.21} \\
\text{C}_2\text{H}_5\text{O}^- \text{(ads)} & \longrightarrow \text{C}_2\text{H}_5\text{O} \text{(g)} + e^- \quad \text{------- 5.22}
\end{align*}$$

The structural features of the nanoscale ferrite complicate the sensing activities, as it involves size, crystallite shape, phase composition, mixed valence and its surface architecture. Gas sensing mechanism of spinel ferrite based sensor belongs to surface controlled resistance mechanism i.e. the change
in resistance is controlled by the species and amount of chemisorbed oxygen on surface of the material. However, the reaction mechanism is quite complex and proceeds through several intermediate steps, which are not yet understood fully. In all type of gas sensing mechanism, oxygen gets adsorbed on the surface of the sensor at desired operating temperature and electron is transferred from conduction band to adsorbed oxygen atom resulting the formation of ionic species such as $O_2^-$ or $2O^-$. The reaction kinetics may be explained by following reactions,

\[
\begin{align*}
O_2^{\text{(gas)}} & \rightarrow O_2^{\text{(ads)}} \quad \text{(5.23)} \\
O_2^{\text{(gas)}} + e^- & \rightarrow O_2^-^{\text{(ads)}} \quad \text{(5.24)} \\
O_2^{\text{(ads)}} + e^- & \rightarrow 2O^-^{\text{(ads)}} \quad \text{(5.25)}
\end{align*}
\]

The electron transfer from the conduction band to the chemisorbed oxygen results in decrease in electron conduction of the sensor. As a consequence, an increase in resistance of the sensor is observed.
Fig. 5.25. Gas response of different test gases for $\text{ZnMn}_{1-x}\text{Cr}_x\text{FeO}_4$ system.
Fig. 5.26 Gas response of Zn$_{1-x}$Cr$_x$FeO$_4$ towards ethanol vapours.

Fig. 5.27. The relationship between the gas response and the concentration of ethanol gas for ZnMn$_{0.25}$Cr$_{0.75}$FeO$_4$
5.3.3.2 Photocatalysis

In recent years, the widespread presence of chemicals such as heavy metals, herbicides, pesticides, aliphatic and aromatic detergents, arsenic compounds, solvents, degreasing agents, volatile organics, and chlorophenols pose a serious threat to the environment. When such chemicals contaminate water sources, they become really hazardous. For instance, waste waters produced from textile and dyestuff industrial processes contain large quantities of azo dyes. It is estimated that 15% of the total dye is lost during dying process and released in waste waters. Oxidation of these organic pollutants at the surface of different metal oxides catalyst is an important photocatalysis application.

Heterogeneous photocatalysis is a process in which a combination of photochemistry and catalysis are operating together. It implies that both light and catalyst are necessary to bring out the chemical reaction. UV light illumination over a semiconductor like metal oxides produces electrons and holes. The valence band holes are powerful oxidants (+1 to +3.5V versus NHE depending on the semiconductor and pH), while the conduction band electrons are good reductants (+0.5 to −1.5V versus NHE). In 1977, Frank and Bard examined the possibilities of decomposing cyanide in water by titania. Since then there is an increasing interest in semiconductor-mediated photo-oxidative processes.

There are number of different semiconducting materials which are readily available, but only few are suitable for sensitizing the photo-mineralization of wide range of pollutants. The semiconductor to be used as photocatalyst for photo-mineralization of wide range of organic pollutants must be (i) photoactive (ii) able to utilize visible and or near UV light (iii) biologically & chemically inert and (iv) photo-stable. It is generally found that only n-type semiconductor oxides are stable towards photo-anodic corrosion, although such oxides usually have bandgaps sufficiently larger than the semiconductors only absorb UV light.
The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants and nearly 10-15% of the dye is lost in the dyeing process and is released in the wastewater which is an important source of environmental contamination. Considerable amount of water is used for dyeing and finishing of fabrics in the textile industries. The wastewater from textile mills causes serious impact on natural water and land in the surrounding area. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems.

The catalytic activity study of the Cr substituted Zn-Mn ferrite photocatalyst was carried by photodegradation rate of thymol blue. The experiment of photocatalytic reaction was conducted in a 100-ml Pyrex glass vessel with magnetic stirring and a UV lamp (8W) with the main wavelength of 253.7 nm. The as-prepared ferrite was used as photocatalyst during the study. It was, therefore, concluded that enhanced photodegradation is directly related to the reduced particle size of the ferrites, which implies photosensitization as the primarily involved process. It is seen from Fig. 5.28 that photocatalytic activity increasing with the increasing substitution of Cr- content. ZnCrFeO₄ shows better photocatalytic activity towards Thymol blue as compared to other Cr substituted ZnMn ferrites.
5.3.3.3 Catalytic study

Oxidation reactions are the most widely observed reactions in the nature. It can happen in living as well as non-living systems. A simple example of this is rusting of iron or reddening of piece of apple when exposed to air. Many biochemical reactions involve the oxidation reactions in many forms such as energy transformation and storage, as well as the biosynthesis and metabolism of essential amino acids, hormones vitamins, etc. Oxidation reactions are involved at some or other step in modern chemical industrial process which are responsible for improvement in standard of living whether it is pharmaceutical industry or polymer industry or the information technology industry. Thus it is difficult to imagine the life without oxidation reactions. The direct single step oxidation of benzylic compounds to carbonyls is a reaction of fundamental synthetic utility.

Fig.5.28. Photocatalytic study ZnMn$_{1-x}$Cr$_x$FeO$_4$ for system
Aromatic carbonyl compounds are widely employed as solvents and intermediates in organic synthesis. Chromic acids and chromium based reagents are versatile oxidizing agents for the benzylic oxidations. Most of methods used to effect this oxidative transformation suffer from drawbacks such as the use of large excess of reagent, solvents, long extraction periods, poor product yield and generation of toxic effluents. Clark et.al have reported catalytic oxidation of ethyl benzenes to acetophenones using alumina supported dichromate. Shaabani et.al have reported the oxidation of alkylaromatics using KMnO\(_4\) supported on ion exchange resins. All the heterogenous catalytic methods mentioned above suffer from drawbacks like difficulty in the preparation and poor reusability in the liquid phase. Hence our objective was to develop a simple, efficient and reusable catalytic system.

To study the catalytic performance of the spinels, oxidation of an oxime (5 mmol) was carried out in the presence of tert-Butyl hydroperoxide (10 mmol) mixing along with 0.1g of ZnMn ferrite as model catalyst and heated to 60°C in oil bath. After completion of reaction, catalyst was separated by filtration and reusability was checked under same reaction conditions. In all these transformation reactions, the progress of the reaction was checked by TLC as well as GC. The product was isolated in ethyl acetate by washing with water and sodium bicarbonate. The isolated products were characterized by GC/MS.

Reaction temperature plays an important role for the completion of reaction. The above studies show that, there is maximum conversion at 60°C. Therefore 60°C is an optimum temperature to get highest yield of product.

To further explore the utilization of the catalysts, oxidation of several oxime compounds was studied using ZnMnFeO\(_4\) as model catalyst and results are summarized in Table 5.14. Data on Oxidation of different oximes using different catalysts are given in Table. 5.15. The results presented in Table indicate ZnCrFeO\(_4\) is the better catalyst for oxidataion process.
Table 5.14. Different oxime oxidation using ZnMnFeO$_4$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>Time (min.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone Oxime</td>
<td>Acetophenone</td>
<td>30</td>
<td>98</td>
</tr>
<tr>
<td>Benzophenone Oxime</td>
<td>Benzophenone</td>
<td>30</td>
<td>95</td>
</tr>
<tr>
<td>3,4 Dimethyl Acetophenone Oxime</td>
<td>3,4 Dimethyl Acetophenone</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>$p$-methoxy benzophenone Oxime</td>
<td>$p$-methoxy benzophenone</td>
<td>30</td>
<td>89</td>
</tr>
<tr>
<td>$p$-nitroacetophenone Oxime</td>
<td>$p$-nitroacetophenone</td>
<td>30</td>
<td>87</td>
</tr>
</tbody>
</table>

Table 5.15. Percentage yield of different oxime oxidation using ZnMn$_{1-x}$Cr$_x$FeO$_4$ system, $x = 0.0, 0.25, 0.50, 0.75$ & $1.0$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>x = 0.0</th>
<th>x = 0.25</th>
<th>x = 0.50</th>
<th>x = 0.75</th>
<th>x = 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetophenone Oxime</td>
<td>96</td>
<td>97</td>
<td>97</td>
<td>96</td>
<td>98</td>
</tr>
<tr>
<td>Benzophenone Oxime</td>
<td>95</td>
<td>96</td>
<td>97</td>
<td>95</td>
<td>98</td>
</tr>
<tr>
<td>3,4 Dimethyl Acetophenone Oxime</td>
<td>90</td>
<td>91</td>
<td>92</td>
<td>89</td>
<td>97</td>
</tr>
<tr>
<td>$p$-methoxy benzophenone Oxime</td>
<td>89</td>
<td>87</td>
<td>88</td>
<td>91</td>
<td>94</td>
</tr>
<tr>
<td>$p$-nitroacetophenone Oxime</td>
<td>87</td>
<td>85</td>
<td>86</td>
<td>88</td>
<td>92</td>
</tr>
</tbody>
</table>
5.3.4 Conclusions

1. Chromium-substituted nanocrystalline Zn-Mn ferrite samples were synthesized by sol-gel autocombustion method.

2. X-ray diffraction studies confirm the cubic spinel structure formation of the samples. The lattice constant and crystallite size decrease with increase of Cr content.

3. Thermal analysis (DTA) confirms the sintering temperature required for spinel phase formation.

4. FTIR spectral studies indicate two absorption bands, one around 600 cm\(^{-1}\) (Tetrahedral) and the other around 500 cm\(^{-1}\) (Octahedral).

5. Scanning Electron micrographs indicate the formation of uniform and fine grained samples.

6. Transmission electron microscopy data revealed that the ferrospinels synthesized by autocombusion method are in nanocrystalline range (~30-40nm) of the ferrite.

7. The content of the metals in the resulting spinel ferrites are close to the theoretical values as shown by EDAX measurements.

8. 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.

9. The ferrites show concentration dependence of ac electrical conductivity.

10. Impedance measurements reveal that the impedance response is dominated by grain boundary behavior.

11. The electrical resistivity is decreasing with increasing temperature for all the samples. This indicates that all the Cr-added ZnMnFeO\(_4\) ferrite have semiconductor-like behavior.

12. Thermoelectric power measurement also confirms that all samples show p-type semiconducting nature.
13. 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.

14. The photocatalytic degradation of thymol blue indicates that ZnCrFeO$_4$ powders can effectively photodegrade thymol blue under ultraviolet plus visible light irradiation.

15. Oxidation of different oximes using different catalysts, indicates that the ZnCrFeO$_4$ is better catalyst.
References


Chapter V: The System ZnMn\textsubscript{1-x}Cr\textsubscript{x}FeO\textsubscript{4}


