
CHAPTER - V

SUMMARY AND CONCLUSIONS

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During the last few decades ferrites have assumed much technological importance especially in electronic industry. Being technologically important they are being extensively studied from the point of view of their electric and magnetic properties to check their suitability for certain applications. The suitability for a certain application is determined by studying crystal structure of a ferrite and its magnetic and electrical properties. Crystal structure is determined by using the techniques of X-ray diffraction, neutron diffraction, Mossbauer spectroscopy etc.

Ferrites with low coercive force are called soft ferrites and those with high coercive force as hard ferrites. In many of the electronic applications for minimising eddy currents and eddy current losses soft ferrites are required. Soft ferrites are having high permeability. The miniaturation can be done by using ferrites with high permeability. The miniaturation of transistor designs, computer designs is possible due to this property. The study of hysteresis loops of ferrites and the squareness ratio is of much importance in magnetic switching and recording devices.

MgFe_2O_4 is a partially inverted ferrite. The addition of Zn^{+2} improves magnetic properties. However, the T_c values are lowered. We have added Zr^{+4} to the system in small amount to study the solid solubility and effect on magnetic properties.

From the point of view of understanding the role of Mg^{+2} and Zr^{+4} ions in influencing the properties of $\text{Zn}_x\text{Mg}_{1-x+t}\text{Zr}_t\text{Fe}_{2-2t}\text{O}_4$ system

systematic studies on characterisation, electrical properties, susceptibility and magnetisation are essential. With this goal in mind the following studies have been carried out.

1. (A) Preparation of $Zr_x Mg_{1-x+t} Zr_t Fe_{2-2t} O_4$,
where $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$ and $t = 0.05$, by ceramic method.
 - (B) X-ray diffraction studies to characterise the ferrite sample.
 - (C) Determination of Curie temperature.
2. D.C. electrical conductivity in the range from room temperature to $600^{\circ}C$ and thermoelectric power to understand the mechanism of conduction and types of carriers that govern the conduction.
3. A.C. magnetic susceptibility to determine whether MD, SD, or SP particles exist in the material and to know the Curie temperature of the samples.
4. Hysteresis studies to determine the saturation magnetisation, coercive field and squareness ratio.

Chapter-I opens with introduction and historical background of ferrites. This is followed by the short account of the spinel ferrites along with the classification of ferrites on the basis of cation distribution. Then general electrical and magnetic properties are discussed. A short account of Neel's theory follows this discussion. Limitation of Neel's theory is pointed out and a brief account of Yafet Kittle theory is given. Finally the general applications are described in brief.

Chapter-II deals with the ceramic technique of the method of preparation of ferrites. The solid state reaction is discussed at the

start. Pellet formation and the possible stages in the preparation technique are explained with the help of flow chart. To confirm the formation of ferrites and characterisation of crystal structure X-ray diffraction studies have been carried out. All samples of $Zn_xMg_{1-x+t}Zr_tFe_{2-2t}O_4$ exhibit cubic spinel structure. The lattice parameter variation obeys Vegard's law which is attributed to the ionic volume difference. The compositional variation of lattice parameter 'a' with the content of Zn exhibits a linear increase from $x = 0$ to $x = 0.6$ and then remains nearly constant. In $Zn_xMg_{1-x+t}Zr_tFe_{2-2t}O_4$ system addition of Zn by x results in decrease of Mg^{+2} content by $(1 - x)$.

Zr^{+4} is substituted in the system and $t = 0.05$, substitution of Zr results in increase of Mg^{+2} content by $[(1-x) + t]$ and decrease in Fe^{+3} content from Fe_2^{+3} to Fe_{2-2t}^{+3}

From the variation of lattice parameter 'a' with the content of Zn, it is seen that the lattice parameter increases with the addition of Zn^{+2} . This can be attributed to the more ionic radius of Zn^{+2} which substitutes Mg^{+2} of less ionic radius.

Comparison of the lattice parameter of $MgFe_2O_4$ ($a = 8.360\text{\AA}$) with that of $Mg_{1.05}Zr_{0.05}Fe_{1.90}O_4$ ($a = 8.418\text{\AA}$) suggests that addition of Zr^{+4} has an effect of increasing the lattice constant.

The effect of substitution of Zr on the lattice parameter can be explained by the combined effect of the cation size 'b' on the repulsion parameter and of the A-site charge on M- the Medelung constant where the lattice parameter is proportional to (b/M) . The entry of tetravalent and higher valence cations in A-sites increases their charge resulting

In the increase in M . When substitution ions are small like $Ti^{+4(1)}$ ($\frac{b}{M}$) decreases. When the ions are larger like Zr^{+4} ($a = 0.80$) an increase in 'b' may offset an increase in M in the initial stages leading to an increase in ($\frac{b}{M}$) and hence in the lattice parameter.

The radii of A and B sites are also calculated. Initially both r_A and r_B increase with the addition of Zn and for $x \gg 0.04$ there is no variation.

The lattice is FCC and unit cell is also confirmed to have number of molecules equal to 8. F.C.C. Bravais lattice is recognised by the fact that all reflections with mixed indices are missing. The values of (h, k, l) are unmixed as evidenced from diffraction pattern. Thus the lattice is F.C.C.

Bond length R_A and R_B also have been calculated. It is observed that R_A increases with increase of Zn content while R_B decreases as the content of Zn increases.

The increase of average bond length R_A can be attributed to the increase in the lattice parameter 'a' with the content of $Zn^{(2)}$. As the content of Zn in the system increases, presence of Zn^{+2} ions on A-site increases. Since $ZnFe_2O_4$ is normal spinel and Zn^{+2} ions occupy A-sites only the bond length R_A increases with more content of Zn^{+2} in the system.

The Curie temperatures for different samples were determined experimentally. The method was similar to that suggested by Larcia⁽³⁾ but with some improvements. Curie temperatures were also computed from susceptibility and conductivity studies. It is seen from all these

that there is a non-linear decrease in the T_c values on addition of Zn in the system. The lowering in T_c can be attributed to the reduction in A-E interaction.

In chapter III studies on electrical conductivity of different samples as well as dispersion of dielectric constant and thermo-emf measurements are reported. Graphs of $\log \rho$ Vs $\frac{10^3}{T}$ are plotted for these samples. These graphs show breaks. It is observed that two breaks, one at 162°C and the other at 315°C occur for sample Zr_2 i.e. for $\text{Zn}_{0.2}\text{Mg}_{0.85}\text{Zr}_{0.05}\text{Fe}_{1.90}\text{O}_4$ sample.

The break at 315°C coincides nicely with the Curie temperature of this sample determined from the experiment as well as $X_{\text{ac}}-T$ studies. The break occurring at 162°C may be due to some impurities present in small traces in the sample. These impurities have not been detected by X-ray analysis which confirms that their percentage is very small. However the impurity conduction can be detected from the temperature variation of Seebeck coefficient.

For remaining samples only one break has been observed in $\log_e \rho$ Vs $\frac{10^3}{T}$ plots. The sample $\text{Zn}_{0.8}\text{Mg}_{0.25}\text{Zr}_{0.05}\text{Fe}_{1.9}\text{O}_4$ does not show Curie temperature and hence this break can also be attributed to impurity conduction. The breaks observed in the rest of the samples coincide nicely with T_c values of these ferrites.

Table 5.1 gives activation energy, interaction energy and Curie temperature of these ferrites. From the values of ΔE given in this table, it is clear that values of ΔE in the ferri and para regions are different which suggests that magnetic ordering change influences the conduction mechanism.

Table 5.1

Curie temperature and activation energy

Sample	Curie temperature			Activation Energy ΔE		Interaction Energy
	Condu-ctivity	Expt	Susce-ptibility	Paramagnetic region	Ferri-magnetic region	
X = .2	315°C	335°C	325°C	0.24 ev	0.34 ev	0.954 ev
X = .4	182°C	200°C	225°C	0.52 ev	0.54 ev	0.407 ev
X = .6	127°C	78°C	150°C	0.52 ev	0.12 ev	0.029 ev
X = .8	-	-	-	0.57 ev	-	-

Compositional variation of ρ for three different temperatures shows almost identical behaviour. It is seen that ρ ($M\Omega\text{cm}$) decreases on addition of Zn^{+2} in the system. This suggests that impedance to the hopping of polarons decreases on addition of Zn^{+2} . Also as the temperature increases the resistivity decreases. This is expected since ferrites are semiconducting in nature.

Dispersion of dielectric constant with frequency from few Hz to MHz range has been studied. It is seen that the dielectric constant decreases as the frequency increases. This type of behaviour is reported⁽⁴⁾ for many ferrites.

From the study of thermo emf presented in table 5.2 it is seen that there is no definite trend exhibited by the compositional variation of Seebeck coefficient ' α ' on addition of Zn in the system. The sign of the Seebeck coefficient indicates that the conduction at room

Table 5.2

Sample	Seebeck Coefficient(α)	Sign
Zr ₁	470	+
Zr ₂	1100	+
Zr ₃	250	+
Zr ₄	120	+
Zr ₅	250	+
Zr ₆	165	+

temperature is governed by electrons. In the case of Zr₆ sample i.e. $\text{Mg}_{0.05}\text{ZnZr}_{0.05}\text{Fe}_{1.9}\text{O}_4$ very interesting behaviour is observed which is reported in table (5.3) It is observed that the sign of ' α ' changes as ΔT is varied. Initially α is -ve suggesting P-type conduction and it becomes +ve when $\Delta T \gg 14^\circ\text{K}$ in which case the conduction is N-type. Basically

Table 5.3

Seebeck Coefficient(α)	T $^\circ\text{K}$	Sign
310	20 $^\circ\text{K}$	+
165	20 $^\circ\text{K}$	+
0	14 $^\circ\text{K}$	+
42.8	80 $^\circ\text{K}$	-

α is created due to difference in the mobilities of the carriers or their densities. The fact that $\alpha = 0$ suggests that at $\Delta T = 14^\circ\text{K}$ whatever difference exists in the mobilities of the carriers or their densities reduces to zero.

In chapter IV studies of susceptibility and magnetisation are reported. We have carried out a.c. magnetic susceptibility studies at various temperatures on the system $\text{Mg}_{1-x+t}\text{Zn}_x\text{Zr}_t\text{Fe}_{2-2t}\text{O}_4$. This was studied at Tata Institute of Fundamental Research (TIFR), Bombay. The variation was recorded on "The Susceptibility and Hysteresis Apparatus Model RM5H - III". From the temperature variation of a.c. susceptibility the following observations have been made.

- (i) For $\text{Mg}_{1.05}\text{Zr}_{0.05}\text{Fe}_{1.9}\text{O}_4$ the normalised a.c. susceptibility increases with the increase of temperature, reaches maximum at 573°K and then decreases with further increase of temperature. $X_{\text{ac}}-T$ behaviour in the case of pure MgFe_2O_4 has been studied previously⁽⁵⁾. There is no peak or cusp observed in this behaviour.
- (ii) When Zn is added to the system, the peaking behaviour is completely suppressed and X_{ac} does not vary significantly with temperature and as the Curie temperature of the sample is approached X_{ac} drops and becomes zero at T_c - the Curie temperature of the sample.
- (iii) The Curie temperature of the sample decreases on addition of Zn in the system. The sample $\text{Zn}_{0.6}\text{Mg}_{0.45}\text{Zr}_{0.05}\text{Fe}_{1.90}\text{O}_4$

tends to exhibit two Tc behaviour. Single Tc in the case of sample indicates that impurity phases detectable by X-ray diffraction studies are not present in the sample.

Magnetisation studies have been carried out on "Hysteresis Loop Tracer" at Indian Institute of Technology (I.I.T.) at Powai, Bombay.

- (i) The variations of M_s and n_E with the content of Zn have been studied. The trend in both the cases is identical. The n_E values first increase with increasing content of Zn upto $x = 0.4$. The increase of Zn content in excess of 40 to 50% appears to decrease n_E value. The n_E value of $MgFe_2O_4$ ⁽⁵⁾ ($n_E = 0.93$) is greater when compared with that of $Mg_{1.05}Zr_{0.95}Fe_{1.90}O_4$ ($n_E = 0.8$) Thus Zr has an effect of reducing the magnetisation.
- (ii) The field variation of M_s for all samples shows that all samples exhibit similar trend. The magnetisation increases with the increase of field initially and after a field of about 800 gauss all the samples saturate.
- (iii) The values of $\frac{M_r}{M_s}$ and H_c decrease on addition of Zinc in the system.
- (iv) The sample with $x = 0$ contains SD particles below $T_b = 300^\circ C$ while above $300^\circ C$ SD-SP transition occurs. The $X_{ac} = 0$ at $T_c = 440^\circ C$. This fact is also supported by the large values of $\frac{M_r}{M_s}$ and H_c for this sample. With addition of Zn the X_{ac}^{-T} does not show peak below T_c and cusp after T_c . X_{ac} is not variable but drops near T_c suggesting that the addition of Zn favours MD types of particles in rest of the samples.

Pure MgFe_2O_4 is reported to have shown presence of M.D. particles. However with the addition Zr there is a peak in $X_{\text{ac}} - T$ variation below T_c . Thus small traces of Zr tend to favour SD types of particles in MgFe_2O_4 . Also addition of Zr lowers n_B . It is suggested by D.C. Khan et. al. that when Zr^{+4} or Ti^{+4} is added in small percentage to Ni-Zn ferrites they occupy A-sites.

In our case of Zr^{+4} going to A-site, just replace Mg^{+2} ions from A-site to B-site. These Mg^{+2} ions going to B-site force, Fe^{+3} ions to A-site resulting in reduction of n_B . MgFe_2O_4 being partially inverted⁽⁶⁾ some Mg^{+2} ions occupy A site also. A number of workers have postulated movement of ions to non-preferred sites; e.g. Zn^{+2} ions to B, Sn^{+4} ions to A and Ti^{+4} ions to A⁽⁷⁾. On the basis of existing predictions⁽⁸⁾ the preferred sites for Ti, Sn, Nb and Ni are B and that for Zn is A.

(vi) α_{YK} increases linearly on addition of Zn. It is seen that as Zn^{+2} is added to the system α_{YK} angles appear and increase with increasing Zn^{+2} content. When Zn^{+2} replaces 60% of Mg^{+2} ions, α_{YK} angles tend to 90° . When the spin arrangement of B-site collapses, leading to vanishing of A-B interactions, α_{YK} angles appear at $x = 0$ and $t = 0.05$. This explains variation of n_B with x .