

CHAPTER - V

SUMMARY AND CONCLUSION

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During the last few decades the studies on ferrites have assumed considerable importance because of their application in electrical, electronic and microwave regimes. As these Materials are technologically important, the same have been studied extensively from the point of view of their magnetic and electrical properties to check their suitability for certain applications. In many electronic applications ferrites with low coercive field and narrow hysteresis loop along with the higher resistivity are required for minimising eddy currents and hysteresis losses. The other important factor in selecting ferrites for certain amount of magnetic effect in applications is permeability. Without any loss on the performance level, the miniaturation can be done by using ferrites with high permeability. In magnetic switching devices the squareness ratio is of prime importance.

Zinc ferrite is reported to be completely normal spinel and its crystal structure is not affected due to conditions of preparation below 1400°C . Copper and magnesium ferrites are partially inverted ferrites and also show variation in the electrical and magnetic properties when heat treated differently. Copper ferrite exhibits tetragonal structure¹ changing semiconducting property² and electrical switching.³ Mixed Ni-Zn and Mg-Zn systems have been studied by many workers.⁴

However, from the point of view of understanding the role of Cu^{+2} ions in influencing the properties of $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ system systematic studies on characterisation, electrical properties, susceptibility and magnetisation are essential. Therefore following studies have been carried out.

- 1) A) Preparation of $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$, where $x = 0, 0.2, 0.4, 0.6, 0.8, 1$ by ceramic method.
 - B) X-ray diffraction studies to characterise the ferrite sample.
 - C) Curie temperature determination.
- 2) 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 temperatures of the samples.
- 4) Hysteresis studies to determine the saturation magnetisation coercive field and squareness ratio.

Chapter I gives account of crystal structure of ferrites, historical and developments of ferrites are followed by Neel's theory. Short account of electrical and magnetic property is also presented. Applications are given at the end. Chapter II gives method of preparation of ferrites, mechanism of solid state reaction and details of pellet formation.

XRD studies have been carried out to confirm the formation of ferrites and characterisation of crystal structure. Except CuFe_2O_4 , all samples of $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ exhibit Cubic structure. CuFe_2O_4 exhibits tetragonal structure. The Lattice parameter variation obeys Vegard's law which is attributed to the ionic volume differences. The value of lattice parameter is minimum for CuFe_2O_4 ($a = 8.251 \text{ \AA}$) and maximum for ZnFe_2O_4 ($a = 8.437 \text{ \AA}$). The lattice is FCC and the number of molecules per unit cell is 8. The materials are single phase as no extra line is deflected in the XRD chart. The radii of the A and B- sites are also calculated. Both r_A and r_B show increase on addition of Zn. Bond lengths R_A and R_B have been calculated. Both R_A and R_B increase on addition of Zn in the system. The increase of average bond length R_A can be associated with the increase in the lattice parameter 'a' with the content of zinc. As the content of Zinc in the system increases, presence 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. Similar explanation holds for the increase of R_B with Zn^{+2} content.

Curie temperatures have been measured experimentally by improving upon the method already suggested by Larida et al.⁵ with the addition of Zinc the T_c values are lowered. The T_c values obtained from the studies of ac magnetic susceptibility and from Gilleo's⁶ Model are compared. The

agreement is satisfactorily between the T_c values obtained experimentally and from ac susceptibility studies. However, theoretical values differ widely indicating that there is a cation migration of Cu^{+2} ions from B-site to A-site. T_c values from Gilleo's Model have been evaluated on the assumption that all Cu^{+2} ions stay on B-site.

In Chapter III studies on thermoelectric power at various temperatures are reported.

1) For CuFe_2O_4 the Seebeck Coefficient is negative upto 300°C indicating that the majority carriers are electrons i.e. the material is n-type. Similar behaviour is exhibited by the samples for which $x = 0.8, 0.6, 0.4$. The following table gives the transition temperature at which Seebeck Coefficient changes its sign.

Table 5.1

Transition and Peak temperature

Sample	Transition Temperature	Peak Temperature
CuFe_2O_4	300°C	127°C
$\text{Cu}_{.8}\text{Zn}_{.2}\text{Fe}_2\text{O}_4$	164°C	-
$\text{Cu}_{.6}\text{Zn}_{.4}\text{Fe}_2\text{O}_4$	152°C	77°C
$\text{Cu}_{.4}\text{Zn}_{.6}\text{Fe}_2\text{O}_4$	90°C	52°C
$\text{Cu}_{.2}\text{Zn}_{.8}\text{Fe}_2\text{O}_4$	-	-

Thus it is seen that with the addition of Zn in the system the transition temperature decreases which bears one to one correspondence with compositional variation of T_c .

Above the transition temperature the samples exhibit p-type of behaviour except for the ferrite $Cu_{.2}Zn_{.8}Fe_2O_4$ which has only positive values of α .

2) Visible peaks are observed during the n-type conduction. These peaking temperature are given in the table (5.1) It is seen that as Zn content increases the value of the peak temperature changes and the peaks also become pronounced. An interesting behaviour is exhibited by the ferrite $Cu_{.8}Zn_{.2}Fe_2O_4$ for which there is no peak and the change of conduction from n-type to P-type is abrupt.

3) In samples of $CuFe_2O_4$, $Cu_{.8}Zn_{.2}Fe_2O_4$ and $Cu_{.6}Zn_{.4}Fe_2O_4$ in the P-region of the conductivity the Seebeck Coefficient shows increase with the increase of temperature without any peaking.

4) In samples of $Cu_{.4}Zn_{.6}Fe_2O_4$ and $Cu_{.2}Zn_{.8}Fe_2O_4$ peaks are observed at the temperatures $177^{\circ}C$ and $52^{\circ}C$ respectively in the P-region conduction.

The observed maxima in α indicate conduction through impurity levels. Mixed conduction takes place in each case and the samples are partly compensated. The variation of α with temperature indicates that variation in charge

concentration plays an important role in conductivity temperature variation.

Addition of Zn^{+2} suppresses the donor centres while the acceptor centres become predominant after the transition temperature. The value of α becomes zero when mobilities or the density of carriers become equal.

In Chapter IV studies on susceptibility and magnetic hysteresis have been reported.

AC susceptibility studies are carried out on the susceptibility and Hysteresis Apparatus mode RMSH-III. The following observations have been made from the temperature variation of X/X_{RT} .

I) Peaks appear in the temperature variation of X/X_{RT} . These peaks are pronounced in the sample S_1 at a temperature of about $225^{\circ}C$ while in the samples S_2 and S_3 the peaks seem to appear at the temperatures $370^{\circ}C$ and $230^{\circ}C$ respectively. No peaks are exhibited by temperature variation of X/X_{RT} in case of samples S_4 , S_5 and S_6 .

II) The peaks appear to be decreasing in intensity with addition of $ZnFe_2O_4$ to $CuFe_2O_4$. The peaks disappears when $ZnFe_2O_4$ is added in excess of 60%.

III) The gradual decrease of T_c on addition of Zinc.

There is a pronounced tendency of single domain in the sample of $CuFe_2O_4$ which is on decrease in the samples

$\text{Cu}_{.8}\text{Zn}_{.2}\text{Fe}_2\text{O}_4$ and $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$.

As the temperature of the sample is reduced from T_c the values of X increase and after the temperature 225°C X shows a decreasing trend. This is due to more and more particles going to single domain state as they go below their respectively T_b , the coercive force increases with decreasing temperature. This fact is also observed experimentally for CuFe_2O_4 . Thus decrease in x below peak temperature is also due to increase in H_c . Similar effect is observed for pure Cobalt ferrite and Zn substituted Cobalt ferrite.

S. Satyanarayana et al⁷ have observed peak at 260°C which is called isotropic peak. This type of the peak⁸ is predominant for samples containing M.D. states. Thus M.D. states are favoured in case of CuFe_2O_4 . The samples $\text{Cu}_{.8}\text{Zn}_{.2}\text{Fe}_2\text{O}_4$ and $\text{Cu}_{.6}\text{Zn}_{.4}\text{Fe}_2\text{O}_4$ which show decreasing peaks exhibit SD + MD states. This is also evidenced by the compositional variation of H_c which decreases on addition of Zn in CuFe_2O_4 , while the sample of $\text{Cu}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ which does not show any peak has MD states only. The sample of ZnFe_2O_4 does not exhibit ferrimagnetic behaviour.

Magnetisation studies have been carried out on "HYSTERESIS LOOP TRACER" supplied by Arun Electronics, Bombay.

The following observations are made from the compositional variation of n_B .

- 1) n_B values increase in addition of Zinc. A decreasing trend is exhibited by this variation when Zinc is added in excess of 50%.
- 2) No n_B values are observed for the samples $Zn_{0.8}Cu_{0.2}Fe_2O_4$ and $ZnFe_2O_4$.
- 3) The H_C values decrease on addition of Zinc.
- 4) α_{yk} increase linearly on addition of Zn.

There is a pronounced tendency for SD in the sample of $CuFe_2O_4$ which is on decrease in the samples $Cu_{.8}Zn_{.2}Fe_2O_4$ and $Cu_{.6}Zn_{.4}Fe_2O_4$. As the temperature of the sample is reduced from T_C the values of X increase and after the temperature $225^\circ C$ X shows a decreasing trend. This is due to more and more particles going to single domain state as they go below their respective T_b , the coercive force increases with decreasing temperature. This fact is also observed experimentally for $CuFe_2O_4$. Thus decrease in X below peak temperature is also due to increase in H_C .

It is seen that as Zn^{+2} is added to $CuFe_2O_4$ the α_{yk} angles appear. These angles increase linearly as the content of Zn is increased and when Zn^{+2} replaces 80% of Cu^{+2} the $y-k$ angles tends to 90° . When spin arrangement of B-site collapses leading to vanishing of A-B interaction. Theoretically as seen in the table (4.1) $y-k$ angles appear at $x = 0.2$ and become 90° when $x = 0.8$. Whatever deviation

exists between α_{yk} and experimental α_{yk} may be due to some transient effects in the measurement of magnetisation due to pulsed field employed or some error in the absolute values of exchange and molecular field constant used for the calculations.

The field variation of magnetisation is given in figure 4.7 for the system $\text{Cu}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 1, 0.8, 0.6, 0.4$). It is seen that similar trend is exhibited by the samples. The saturation magnetisation for all the samples is clearly seen and the trend is similar to compositional variation of ~~variation of~~ n_B at a constant field.

Notes and References

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