EFFECT OF TETRAVALENT IMPURITIES ON THE MICROSTRUCTURAL, MAGNETIC AND ELECTRICAL PROPERTIES OF $Ni_{0.58}\ Zn_{0.40}\ Fe_{2.04}\ O_{4+\delta}$ FERRITE SYSTEM

A THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
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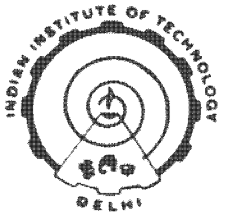

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DECLARATION

This is to certify that the thesis, entitled "Effect of tetravalent impurities on the microstructural, magnetic and electrical properties of $Ni_{0.58}Zn_{0.40}Fe_{2.04}O_{4+\delta}$ ferrite system", being submitted by Mr. Satbir Singh to the Department of Physics Indian Institute of Technology, Delhi for the award of the Degree of Doctor of Philosophy is a record of bonafide research work carried out by him. He has fulfilled the requirements for the submission of this Thesis, which in our opinion has reached the requisite standard.

The results contained in this work have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

24/1/86

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PREFACE

The properties of various ferrites are generally modified and upgraded by substituting optimum amounts of various impurity ions in basic ferrites. Some of their properties like permeability, magnetic losses, electrical resistivity and coercive force are also affected by the grain size, porosity and inclusions in the matrix. Incorporation of tetra- or penta-valent ions in the ferrite matrix causes localization of the Fe^{2+} ions preventing them from taking part in the electrical conduction. They also change the cation vacancy concentration leading many times to a change in densification and grain growth kinetics.

A number of workers have studied the effect of doping trivalent, tetravalent or pentavalent impurities into the Ni-Zn ferrite and the distribution of ions on the tetrahedral and octahedral spinel sites of this ferrite system is more or less established. The addition of tetravalent impurities like SiO_2, GeO_2, or SnO_2 in the Ni-Zn ferrite is of particular interest as it reportedly leads to coarse crystallization and grain growth. A detailed study of the effect of these additives on the sintering kinetics and grain growth of this ferrite system is not yet available.

The aim of the present work is to experimentally study the magnetic and other physical properties of Ni-Zn ferrite of a standard composition of commercial interest substituted with Si^{4+} ions of ionic radius 0.42 Å, Ge^{4+} ions of ionic radius 0.53 Å and Sn^{4+} ions of ionic radius 0.71 Å separately with successively increasing concentrations. It has also been the purpose of these studies to see if the Globus model of grain

size limited domain wall could be applied to these doped ferrites Accordingly, three series of polycrystalline ferrite samples of the following composition were prepared by the standard ceramic technique for carrying out the above named studies.

$$Ni_{0.58}Zn_{0.40}Fe_{2.04}O_{4+\delta} + x(MeO_2)$$

Where MeO_2 is one of the three oxides $SiO_2/GeO_2/SnO_2$ and x varies in eight steps from 0.0000 to 0.0128. δ is the excess oxygen.

This work is divided into five chapters which are briefly escribed as follows.

The first chapter provides the relevant theoretical background and experimental techniques for the studies undertaken. A summary of the classical model of magnetization mechanism in soft ferrites and the Globus model has been included to illustrate the basic differences between the two. A brief discussion on grain growth kinetics has also been included.

The second chapter comprises of two parts. The first part deals with the preparation methodology to achieve the required consistency of sample quality. The second part deals with the sample characterization. The limits of impurity dissolution were studied by X-ray microprobe analysis, Auger spectroscopy and μ-T measurements. Chemical analysis of segregated phases was conducted through the Scanning Electron Microscope used in the EDS mode. It has been concluded that $SiO_2/GeO_2/SnO_2$ have increasing solubility in the Ni-Zn ferrite in that order, as predicted from their ionic radii. SiO_2 has negligible solubility in the ferrite matrix. Even if some solubility exists, it is not possible to locate the solubility limit since the raw

materials used themselves contained silica (upto 0.02 percent) as a natural impurity. SnO_2 on the other hand has an ionic radius comparable in size to the cations in the host lattice and its solubility limit lies far beyond the highest dopant concentration tried in the present studies. GeO_2 is found to have a solubility limit upto 0.32 mole %.

In chapter three, the results of the present studies on the grain growth and densification of ferrite samples as a function of impurity concentration and sintering time have been presented and discussed. It has been concluded that the SnO_2 doped samples upto the highest concentration level follow the Burke's model of impurity limited grain growth as given by

$$D_f^2 \left(\frac{D_o - D}{D_f} + \text{Ln} \frac{D_f - D_o}{D_f - D}\right) = kt$$

Where D_f is the limiting grain diameter, D_o the initial particle size, D is the average grain diameter of the sintered sample, k is the rate constant and t is the sintering time.

In the case of SiO_2/GeO_2 doped sample (at >0.64 mole %) the activation energy of grain growth decreases to $\sim$55 kcal/mole which suggests sintering in the presence of aliquid phase. The data is found to be obeying Lay's relationship for liquid phase sintering given by

$$D^3 - D_o^3 = kt$$

The fourth chapter presents the magnetic and electrical properties, that is, the initial permeability, magnetic loss, disaccomodation and electrical conductivity of the three sample series. The initial permeability changes in the case of SiO_2/

GeO_2 doped samples are attributed to the microstructure developed by the discretely segregated SiO_2 phase and a uniform precipitation of undissolved GeO_2 around the grains. The addition of SnO_2/GeO_2 produces three disaccomodation peaks in the thermal spectra of disaccomodation. The relaxation peak III has been found to split into two processes III' and III. These peaks (namely III', III and II) are attributed to the relaxation of Fe^{2+} - $\square$ pairs localized by Me^{4+} ions, Fe^{2+} - $\square$ pairs and Fe^{2+} -Fe^{2+} pairs respectively. The d.c. conductivity at room temperature of SiO_2 doped sample (containing $\geq$0.64 mole%) show a decrease of several orders of magnitude from the average value of $\sim 10^{-3}\ \Omega^{-1}cm^{-1}$. These results are attributed to the existence of two parallel conduction mechanisms dominant at two different temperature ranges.

The fifth chapter relates to the analysis of the minor hysteresis loops of the three sample series obtained by using an electronic B-H loop recording system fabricated for these studies by the author. It has been concluded that even when there is significant magnetic inhomogeneity in the material the Globus model of magnetisation mechanism is applicable and the minor B-H loop areas can be related to the magnetic parameters and grain size as per this model.

Finally, the main conclusions from this study have been summarized in the sixth chapter.

I N D E X

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