Chapter VI

Summary
SUMMARY

Chemical combustion method chiefly and hydrothermal technique has been adopted to prepare pure NiFe$_2$O$_4$, Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$, Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$/SrFe$_2$O$_4$ and Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$/BaTiO$_3$. Though these techniques are simple but cannot be used without thorough knowledge of Chemistry. It has been observed that role of methodology is crucial factor for the change in morphology and associated properties.

Increase in average size of the particles with the annealing temperature was observed in case of NiFe$_2$O$_4$, when prepared by chemical combustion method and annealed at different temperatures. XRD diffraction shows the spinel phase with Fd3m space group and the average values of particles size using Scherer formula are 16, 17, 21 and 25 nm, respectively, with 400 °C, 500 °C, 600 °C and 700 °C.

The values of ε are 16, 27, 38 and 42 with frequency of 1 MHz, and dispersionless dielectric response up to 5, 17, 10 and 3 MHz, respectively, for NF with 400 °C, 500 °C, 600 °C and 700 °C. The values of saturation magnetization depend upon size of nanoparticles and show better results at low annealing of 500 °C. The results of magnetic and electrical measurements are explained on the basis of Nano sized by grains and boundary effect by cole-cole model of impedance spectroscopy.

Sample prepared at 500 °C of NiFe$_2$O$_4$ was best among four samples. The substitution of Zinc for Nickel ions brought appreciable changes in the structural, electrical and magnetic properties of Ni$_{1-x}$Zn$_x$Fe$_2$O$_4$ [ x = 0.0, 0.20, 0.25, 0.30, 0.35, 0.40 and 0.50] when prepared by chemical combustion method. XRD pattern shows the formation of cubic spinel phase with the values of lattice constant increasing linearly with increasing Zn$^{2+}$ content. The values of average particles sizes are measured by Scherer relations and are consistent with TEM analysis.

Saturation magnetization increased up to x = 0.40 and then decreased with the increase in Zn concentration. This trend in saturation magnetization has been explained on the basis of Neel two sub-lattice models. All the NZF samples show good ferromagnetism and the highest value of ferromagnetism observed in NZF40, i.e., Ms ~ 80.63 and Mr ~ 27.6 emu/g and low Hc ~ 154.11 Oe. The frequency

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dependent dielectric measurements show Nano size dependent values of dielectric constant and tanδ. From the findings sample with 40% of Zinc doping was found to be the best sample and was chosen on this ground for further study.

Saturation magnetization value of pure NiFe₂O₄ and doped with x = 0.40 has been very much convincing. Sample prepared at 500 °C of NiFe₂O₄ and with x = 0.40, has been chosen for further research by hydrothermal method and for preparation of hard and soft composite along with composite of multiferroic.

The NF and NZF ferrite were prepared by employing hydrothermal synthesis route. Homogenous and uniform Nanoparticles were formed in case of NF and formation of nanowires has been observed in case of NZF. Formation of nanowires led to the speculations about growth mechanism in the formation of nanoparticles of HNF and nanowires in the case of HNZF.

The mechanism is described on the basis of aggregation of metal with OH ions by larger surface energy, and ionic radii difference among these which involves oriented attachment due to Ostwald ripening process during hydrothermal treatment. X-ray diffraction analysis results confirm the formation of cubic spinel phase of HNF and HNZF ferrite. The values of Magnetic results for Ms are 35.78 and 54.89 emu/g, Mr 2.01 and 3.03 emu/g and Hc 26.13 and 33.86 Oe respectively, measured for HNF and HNZF samples.

The improvement in dielectric polarization and values (At frequency of 10 MHz the values of dielectric constant are 60 and 91 for HNF and HNZF) at higher frequency is explained on the grounds of size dependent nanostructure. The compressive stress induced by surface curvature of nanowire results an effective tensile in the length direction leads to a large off-centre displacement which enhances the polarization.

The best sample from previous section (HNZF) was selected for preparation of hard and soft composite by adding SrFe₂O₄ as hard component in the Ni(0.06)Zn(0.40)Fe₂O₄. Both the methods were used to synthesis of these samples to evaluate difference in properties due to preparative methodology.

From the values of X-Ray diffraction studies lattice constant was calculated and found to be 8.478/8.018 and 8.421/8.027 respectively for CNZF/SF and
HNZF/SF samples. The sizes so obtained from the X-ray data is confirmed by the TEM micrograph analysis and are 22 nm for CNZF/SF and 6 nm with length of 160 nm for the sample prepared by hydrothermal technique.

Magnetic measurements also suggest HNZF/SF as better sample with good values. The values of Ms are 27.20 emu/g and 52.36 emu/g, $M_r$ are 19.38 and 41.41 (emu/g) and for Hc 190 and 203.89 (Oe) for the CNZF/SF and HNZF/SF samples prepared by chemical combustion method and hydrothermal synthesis route. Values for the dielectric measurements conducted at 10 MHz are found to be 27 and 125 respectively for CNZF/SF and HNZF/SF samples.

Multifunctionality of magnetoelectric (ME) multiferroic (MF) materials have provided significant potentials for applications such as spintronics, memory, sensors, etc. to the next generation multifunctional devices. This led us to synthesise best ferrite sample as multiferroic composite.

The MF NZF/BT composite has been successfully prepared by chemical combustion and hydrothermal synthesis routes. It has been observed from the morphological results that there has been again a set of different mechanisms followed by CNZF/BT and HNZF/BT samples because of different preparative methodology.

The growth mechanism of the formation of small nanoparticles of CNZF/BT is probably due to unavailability of ageing time which probably led to no Ostwald ripening along with no aggregation mechanism similar to CNZF/SF. The nanowires of HNZF/BT were formed due to Ostwald ripening process during hydrothermal treatment. XRD analysis results support the formation of spinel cubic phase of NZF and tetragonal polycrystalline of BT.

The TEM images show average nanoparticles size 4 nm of CNZF/BT while nanowires of diameter 3 nm and length > 150 nm. The value of $P_s = 16.51$ and 24.37 $\mu$C/cm$^2$, and $P_r = 7.54$ and 11.78 $\mu$C/cm$^2$, and $E_c = 13.97$ and 15.54 kV/cm, respectively was observed for CNZF/BT and HNZF/BT composite.

The values of Ms are 12.26 and 18.35 emu/g respectively, measured for CNZF/BT and HNZF/BT composite. The maximum value of $\alpha E$ is 78.57 and 102.54
mV/cm Oe, respectively, for CNZF/BT and HNZF/BT MF. The $\varepsilon_r$ at 10 MHz of frequency is 31 and 55, respectively, for CNZF/BT and HNZF/BT nanostructures.

From the results it is clearly evident that samples prepared by hydrothermal method have edge over chemical combustion method samples. This can be attributed to probability of formation of different nanostructure with different morphologies and properties associated with it.