Chapter V

Discussion
DISCUSSION: STRUCTURAL, MICROSTRUCTURAL, MAGNETIC, DIELECTRIC AND OPTICAL PROPERTIES OF NiFe$_2$O$_4$, Ni$_{(1-X)}$Zn$_{X}$Fe$_2$O$_4$ AND NiFe$_2$O$_4$/SrFe$_2$O$_4$, Ni$_{(0.6)}$Zn$_{(0.4)}$Fe$_2$O$_4$/SrFe$_2$O$_4$ NANOSTRUCTURES.

INTRODUCTION:

In this section of the thesis, discussion is presented on results of materials listed in chapter 4.

5.1 NiFe$_2$O$_4$ nanostructures synthesized via chemical combustion method:

5.1.1 Structural, microstructural, magnetic and dielectric studies of NiFe$_2$O$_4$ (NF):

Figure 4.1(a) shows the XRD pattern of NF samples annealed at various temperatures, 400°C, 500°C, 600°C and 700°C. As seen, NF with the spinel structure has been formed at 400°C with minor impurity peaks. However, a polycrystalline spinel phase is formed with 500°C. It was noted that a small amount of α-Fe$_2$O$_3$ phase had also been formed with 600°C and 700°C.

It was found that there is no significant change in the lattice parameter (a) values of the samples thermally treated at various temperatures. Thus, independent of the annealing temperature, the (a) values of NF samples with various crystallite sizes are close to the lattice parameter of bulk NF (8.170 Å). But there was change observed in crystallize size of samples as the size increased with increase in temperature (Fig. 4.1(b)). The broad XRD line indicates that the ferrite particles are Nano-size. From the peaks and calculated sizes it was observed that sizes increase with annealing temperature [Fig. 4.1(b)]. So obtained crystallographic patterns reveal a cubic spinel ferrites phase with good crystallinity and broad peaks due to smaller Nano particle size.

The FT-IR spectrum of the NiFe$_2$O$_4$ prepared at 500°C is presented in Fig. 4.2. Spectrum shows characteristic absorption bands of cubic spinel structure. The IR
band \((V_1)\) generally observed in the range of 600-550 cm\(^{-1}\), corresponds to intrinsic stretching vibrations of the metal atom at the tetrahedral site \(\text{M}_{\text{tetra}} - \text{O}\), whereas the IR band \((V_2)\) is usually observed in the range of 450 – 380 cm\(^{-1}\) assigned to the octahedrally – bonded metal atom \(\text{M}_{\text{octa}} - \text{O}\).

Figure 4.3 shows the Transmission Electron Microscopy images for NF samples annealed at 400 °C, 500 °C, 600 °C and 700 °C. In general all micrographs show homogeneity and uniformity except with 400°C of little amorphous behaviour. It is seen that with the increase in annealing temperature, the average grains size increases. Also on comparison it was observed that the values of particles size are consistent with those measured by the XRD.

The magnetization hysteresis loops recorded at room temperature for the NF with different annealing temperatures (400 °C, 500 °C, 600 °C and 700 °C) is shown in Fig. 4.4. It is well known fact that magnetism originates from the spin of unpaired electrons. In ferrite lattice cations are separated by oxygen anion. From electronic configuration, O\(^{2-}\) has no magnetic moment since it has completely filled shells, with p-type outermost orbitals. Ni\(^{2+}\) (d\(^8\)), Zn\(^{2+}\) (d\(^{10}\)) and Fe\(^{3+}\) (d\(^5\)) cations of the ferrite have 1, 0 and 5 unpaired electrons respectively. Zn\(^{2+}\) being diamagnetic, the outer sub-shell of it is completely filled. So divalent Ni and trivalent Fe have magnetic moments due to unfilled 3d sub-shell. The measured values presented in table 4.1 do confirm these facts.

It is observed that NF with 500°C has similar values of \(M_s\) and \(H_c\) and \(\mu_B\) than with 600° and 700°C but with a large \(M_r\) value. Generally, the grains size increases with increasing annealing temperature and shows higher magnetization. But the occurrence of magnetic behaviour in our specimens of NF may be due to two reasons: Firstly, related with drastic nickel loss at higher temperatures (extra peaks seen at 600° and 700°C annealing in XRD). Secondly it may be due to the occurrence of superparamagnetic state when the particles size lies in Nano scale [Verma et al. 2010].

Figure 4.5 shows the frequency dependence of dielectric constant \((\varepsilon)\) and loss factor \((\tan\delta)\) [inset] for all the samples. The dielectric constant \(\varepsilon\) decreases with the grain size reduction. The variations in the dielectric constant of ferrites are mainly
attributed to the variations in the concentration of Fe$^{2+}$ ions [Irvine et al. 1990; Koops et al. 1951]. Hence, polarization and dielectric constant are expected to increase with the concentration of Fe$^{2+}$. Moreover, there are also reports [Kaur et al. 2012; Dube 1970] of a decrease in dielectric constant with a decrease in particle size. In the present studies, for the lower grain size (16 nm), there is a migration of some of the Fe$^{3+}$ ions from octahedral $[B]$ to tetrahedral $(A)$ sites, which is clearly evident from the in-field Mossbauer studies [Dube 1970].

Therefore, the dielectric constant $\varepsilon$ is lower for the 400°C annealed (16 nm) sample compared to that of the as-prepared sample 700°C (25 nm). In the present sample, $\varepsilon$ shows initially decrease with increase in the frequency. The presence of Ni$^{3+}$ and Ni$^{2+}$ ions in $B$ sites gives rise to $p$-type carriers which also contribute to the net polarization in addition to the $n$-type carriers. However, the contribution of the $p$-type carriers should be smaller than that from the $n$-type carriers with an opposite sign. Since the $p$-type carriers have a lower mobility than the $n$-type carriers, the contribution to polarization from the former will decrease more rapidly even at low frequencies than the latter.

As a consequence, the net contribution will increase initially and then decrease with frequency as observed in the present samples. Rezlescu et al. [1974] has also reported a similar behaviour in the case of Cu-Ni ferrites. Fig. 4.5 (inset) shows the plot between dielectric loss (tan$\delta$) and frequency. The value of tan$\delta$ decreases with frequency for all the grain sizes. The decrease in tan$\delta$ takes place when the jumping rate of charge carriers lags behind the alternating electric field beyond a certain critical frequency. High temperature annealing leads to the escape of Fe$^{2+}$ ions from the lattice, which results in greater structural imperfections and high dielectric losses.

Fig. 4.6 is the plot (Impedance Spectroscopy) of $Z'$ versus $Z''$ (Nyquist or Cole-Cole plots) taken over a wide frequency range (20 Hz to 20 MHz) at temperature of 500 K. The obtained result is indicative of non-Debye type relaxation and it also manifests that there is a distribution of relaxation time instead of a single relaxation time in the material [Verma et al. 2010]. The values of resistance of grains ($R_g$) and boundaries ($R_{gb}$) have been obtained from the intercept of the semi-circular arcs on the real axis ($Z'$). The values of resistance of grain boundaries, $R_{gb}$ is higher than
grains, $R_g$ indicates that the effect of grain boundaries is dominant on electrical and magnetic properties when the size of nanoparticles is quite small.

5.2 Ni$_{(1-X)}$ Zn$_{(X)}$ Fe$_2$O$_4$ nanostructures sintered at 500 °C synthesized via chemical combustion method:

5.2.1 Structural, microstructural, magnetic and electrical properties of Ni$_{(1-X)}$ Zn$_{(X)}$ Fe$_2$O$_4$ nanostructures:

Figure 4.7 shows the FTIR spectra of NZF ferrite nanoparticles carried in the range of 400–3500 cm$^{-1}$ for the samples sintered at 500 °C for 5 hrs. These FTIR results confirm that Ni$^{2+}$ is stabilized in the octahedral crystal field whereas Zn$^{2+}$ prefers tetrahedral sites. The spectrum also shows evidence of presence of very light bands of CO$_3^{2-}$ and NO$_3^{-}$ and moisture. The band at 3433.31 cm$^{-1}$ and $\sim$1600.12 are due to stretching and deforming vibrations of OH$^-$ groups and 2300.00 and 1000.00 cm$^{-1}$ correspond to traces of atmospheric or adsorbed CO$_3^{2-}$ and nitrate ions respectively.

Figure 4.8 (a) show the XRD pattern of NZF ferrites heated at 500 °C/5 h. It’s been observed that with the increase of Zinc percentage value of lattice constant (a) also increases from 8.15 – 8.391 Å [Figure 4.8(b)]. The increase in lattice constant is attributed to migration of Fe$^{3+}$ from (A) site to (B) site due to Zn$^{2+}$ addition in NiFe$_2$O$_4$. As Zn$^{2+}$ ions are larger (0.82) Å as compare to Fe$^{3+}$ (0.67) Å, their replacement results into expansion of lattice in turn lattice parameter.

From the calculated results (table 4.2) of theoretical density it is observed that it is slightly higher than the experimental density. This is due to the existence of small porosity in the samples, which depends upon the sintering conditions.

Microstructure studies (Fig.4.9) show that the doping of Zn$^{2+}$ (ionic a radius of Zn$^{2+}$ is greater than Ni$^{2+}$) promotes ferrite grain growth. According to the behaviour exhibited in Fig. 4.9, samples with $x = 0$ shows a homogeneous microstructure with small grain size and a uniform size distribution. As the concentration of Zn$^{2+}$ increases ($x \geq 0.1$) grain growth was observed due to the increment in lattice constant “a” is confirmed by XRD pattern.
The magnetization hysteresis loops recorded at room temperature for the NZF are shown in Fig. 4.10. It has been observed that the magnetic measurement shows enhancement in the value of saturation magnetization \(M_s\) with increasing \(\text{Zn}^{2+}\) substitution up to 40% and then it shows decline. The values of \(M_s\), \(M_r\) and \(H_c\) are also given in table 4.2. In the present study, the maximum \(M_s\) has been observed for the composition \(\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4\) which is comparable to the bulk material which reports the maximum \(M_s\) for \(\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\) [Verma et al. 2011]. However, except \(x = 0.1\), the values of \(M_s\) are found to increases with \(\text{Zn}^{2+}\) ions, which is explained on the basis of Neel’ theory of ferrimagnetism.

When the concentration of \(\text{Zn}^{2+}\) ions increases, it must occupy sites which result into reduction in the value of \(M_A\). However \(M_B\) will remain unchanged and therefore the value of net magnetization \(M_s\) will be increases. But with higher concentration of \(\text{Zn}^{2+}\) ions \((x > 0.4)\), \(A-B\) interaction becomes weak and \(B-B\) interaction become strong which consequences the decrease in values of \(M_s\) [Verma et al. 2011]. In addition, with low concentration of \(\text{Zn}^{2+}\) \((x\leq0.1)\) \(M_s\) decrease because in result of the fact that \(\text{Fe}^{3+}\) ions will have no magnetic neighbour at this percentage and spins become uncoupled which leads to the decrease in saturation magnetization as shown by NZF0 in Fig.4.10

The variation in the value of \(\mu_B\) may be related with preparation technique and change in magnetic interaction takes place by alteration of cations distribution at tetrahedral and octahedral sites with doping of \(\text{Zn}^{2+}\) in \(\text{NiFe}_2\text{O}_4\) ferrite. Upon critical comparison of all samples, it was observed that the best sample with enhanced \(M_s\) has been found to be NZF40 \([\text{Ni}_{(0.60)}\text{Zn}_{(0.40)}\text{Fe}_2\text{O}_4]\) and before it and after it saturation magnetization value is less than this sample.

There are several structural and microstructural parameters which contributes the dielectric properties in ferrites. Figure 4.11 shows the variation of relative dielectric permittivity \(\varepsilon_r\) and loss factor \((\tan\delta)\) with frequency measured at room temperature. From the values the observed dielectric behaviour is similar as reported by Javed Iqbal et al. [2010] for their system nanoparticles of Ca-substituted strontium hexaferrite. The dielectric constant decreases rapidly in low frequency region and the rate of decrease is slow in high frequency region, the behaviour almost approaches to frequency independent behaviour. The dielectric loss \((\tan\delta)\) is found to decrease faster
than $\varepsilon_r$ in the low frequency region and the variation is same as $\varepsilon_r$ in higher frequency region.

It is also seen from Fig.4.11 that the variation in the value of dielectric constant might be due to increasing of particles size and concentration of Zn$^{2+}$ ions in NiFe$_2$O$_4$. In Nano materials, there is an additional chance of having a small dielectric constant because of large grain boundaries owing to the large dc resistivity. Samples of Nano-sized particles contain a relatively larger volume fraction of grain boundary atoms because of the decrease in the size of particles, the large insulating boundaries result. The insulating boundaries act as a barrier for current conduction between particles, resulting into an increase in the value of dc resistivity [Verma et al. 2012]. In addition, according to Bellad et al. [2000], the polarization in ferrites is through a mechanism similar to the conduction process.

The polarization declines with rise in frequency and then reaches a constant value due to the fact that beyond a certain frequency of external field, the electron exchange between Fe$^{2+}$ and Fe$^{3+}$ cannot follow the alternating field. The large value of $\varepsilon_r$ at lower frequency is due to the prevalence of species like Fe$^{2+}$ ions, interfacial dislocations pile ups, oxygen vacancies, grain boundary defects, etc. However the decrease in $\varepsilon_r$ with frequency is natural because of the fact that any species contributing to polarizability delay behind the applied field at higher and higher frequencies. Substitution of Zn content results into decrease in the number and the mobility of holes and hence results in a decrease in the values of dielectric constant.

### 5.3 Hydrothermal synthesis of best sample from NF series (NF 500 °C) and NZF series NZF40 (Ni$_{(0.6)}$Zn$_{(0.4)}$Fe$_2$O$_4$):

#### 5.3.1 Structural, microstructural, magnetic and electrical properties of NF 500 °C and NZF40 Ni$_{(0.6)}$Zn$_{(0.4)}$Fe$_2$O$_4$ nanostructures:

Fig.4.12 shows the XRD pattern of NF and NZF nanostructures synthesized by hydrothermal method at 180 °C/48h. In both NF and NZF the major Bragg’s peaks for cubic spinel are observed. It shows characteristic peaks of cubic spinel with Fd3m space group in both samples. From the values of the lattice parameter and Dx value, it was observed that both increase with the introduction of Zinc dopant NF and NZF samples.
Also the crystallite size of sample with zinc increases which confirms incorporation of Zinc. The ionic radius of Zinc is more than the Nickel, so increase in all parameter is observed. The broadening of the full width at half maxima of the diffraction peaks indicates the formation of nanocrystalline products. The average crystallite sizes were calculated from the XRD data using Debye Scherer formula are 20 and 24 for NF and NZF samples.

Fig. 4.13 shows FTIR absorption spectra of nanocrystalline NF and NZF samples prepared without surfactant which was recorded in the range of 4000 – 400 cm⁻¹. On the basis of reported literature, all spinel’s and particularly in ferrites metal oxygen bands are seen in the spectrum of FTIR. Characteristic bands so obtained for NF and NZF corresponds to intrinsic stretching vibrations of the metal at tetrahedral site, $M_{\text{tetra}}$-O and Octahedral metal stretching vibrations $M_{\text{octa}}$ – O. The spectrum also shows evidence of presence free or absorbed water.

Fig. 4.14 shows the Tem images of samples (NF and NZF). From the Tem micrographs, it is clear that the nanostructures obtained at different magnification are consisting of nanoparticles of very small size having a cubic like faces in case of NF, whereas in case of NZF nanowires like structures consist of large number nanowires is seen in the Tem images. The growth mechanism of their formation is explained as under:

The growth mechanism in the formation of nanoparticles and nanowires of NF and NZF by hydrothermal reactions tracks a liquid nucleation system. The principle involved chemical kinetics, theories of chemical equilibrium, and thermodynamic properties of water systems under hydrothermal conditions. Few researchers have proposed dissolution-precipitation process by mechanism [Eckert et al. 1996] on the basis small crystalline nuclei in a suspension which is supersaturated and then it is monitored by crystal growth, in which the bigger particles will grow at the cost of the small ones owing to the energy difference between large particles and the smaller particles [Kubota et al. 1997].

Homogenous mixture of solution of metal chlorides when interact with OH⁻ ions of KOH at pH 13 behave differently. In the case of NF, Ni when reacts with OH⁻ forms Ni(OH)₂ readily undergoes oxidation to Ni oxyhydroxide, NiOOH, in combination with a reduction reaction, often of a metal hydride given as:
These reactions confirm no aggregation of particles in case of Ni—OH⁻ ion interactions. Probably due to smaller ionic radius and surface free energy difference among ions. Whereas in case of NZF, Zn when come in contact with OH⁻ forms aggregates given as:

\[
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2
\]  

(3)

\[
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^{2-}
\]  

(4)

The equation (4) leading to chain like aggregates, this approach may be attributed to large ionic radius and surface free energy difference among precursors.

In the case of NF, the crystal growth is splitting into nanoparticles and no oriental attachment because Ni inactivity in formation of aggregates with OH⁻ ions. Thick wire formation is observed in NZF, which could be attributed to aggregation of Zn with OH⁻ ions. Oriental attachment in one crystallographic direction has led to their formation of thick wires.

Fig.4.15 shows the ferromagnetic behaviours of NF and NZF ferrites by measuring M-H hysteresis at room temperature. In case of NiFe₂O₄, the value of magnetic moment exist due to distribution of Fe³⁺ ion on tetrahedral sites (A) and presence of Ni²⁺ and Fe³⁺ ions on octahedral (B) sites. In the Ni₁(0.6)Zn₁(0.4)Fe₂O₄(NZF), Zn²⁺ ions displace few of Fe³⁺ ions from tetrahedral (A) sites to octahedral (B) sites leading to overall increase in magnetic moment value.

The dielectric constant (Ɛr) and loss (tanδ) measurements in the frequency range of 100 Hz to 1 MHz is given in the Fig. 4.16. It is seen that the value of Ɛr decreases with increasing frequency and at further higher frequencies it becomes slight variable. At lower frequency, the dispersion in dielectric constant is due to interfacial polarization. At higher frequencies due to rotational displacements of the dipoles which results in the orientational polarization, dispersion in dielectric constant becomes small approaches nearly frequency independent response.
The observed behaviour of the dielectric dispersion can be explained on the basis of Koops theory [Koops 1951] and Maxwell-Wagner interfacial type of polarization [Wagner et al. 1913]. In this model, a ferrite material is assumed to consist of well-conducting grains separated by less conducting grain boundaries. The electrons reach the grain boundary through hopping and if the resistance of the grain boundaries is high enough, electrons pile up at the grain boundaries and produce polarization. However, as the frequency of the applied field is increased, the electrons reverse their direction of motion more often.

The higher value of $\varepsilon_r$ in the case of NZF depends upon the type of nanostructure, i.e., nanoparticles in case of NF and nanowires in NZF (large surface to volume ratio in the case of nanowires than nanoparticles). The enhancement in polarization is adopting by an axial polarization (the preferred polarization direction dictated by geometry) [Pilania et al. 2009].

5.4 Hydrothermal and chemical combustion synthesis of NZF40 $\text{Ni}_{(0.6)}\text{Zn}_{(0.4)}\text{Fe}_2\text{O}_4$ with SrFe$_2$O$_4$:

5.4.1 Structural, microstructural, magnetic and electrical properties of NZF40 $(\text{Ni}_{(0.6)}\text{Zn}_{(0.4)}\text{Fe}_2\text{O}_4)$ with SrFe$_2$O$_4$ nanostructures:

Figure 4.17 shows the XRD pattern of (CNZF/SF) and (HNZF/SF) nanostructures prepared by using chemical combustion and hydrothermal methodology. The material so produced is polycrystalline in nature. From XRD diffraction data composite formation is confirmed as characteristic miller indices of NZF and the orthorhombic phase of SrFe$_2$O$_4$ ferrites with Miller indices are in accordance with JPCDS Data Card no. 48-0156 (for SrFe$_2$O$_4$). The broadening of the full width at half maxima of the diffraction peaks indicates the formation of nanocrystalline products. The lattice constant values are well consistent with reported literature for CNZF/SF and HNZF/SF Nanocomposites. The crystallite sizes found to very small for sample prepared by hydrothermal.

Fig. 4.18 reveals the TEM images at different magnification of CNZF/SF and HNZF/SF composites respectively. From the TEM micrographs, it is confirmed that
sample prepared (HNZF/SF) by using hydrothermal method has smaller size and also are in the form of nanowires. Whereas, small size cubic like faces with larger diameter compare to HNZF/SF has been observed in the case of CNZF/SF. This variation in size shows role of methodology is very crucial in deciding change in morphology. A possible mechanism of Nanowire formation in case of HNZF/SF is presented as under:

The growth mechanism in the formation of nanoparticles and nanowires of CNZF/SF and HNZF/SF by chemical combustion method and hydrothermal reactions follow different routes. Particularly hydrothermal method tracks a liquid nucleation system. Though a lot of work in this concern has been done still a lot of work is needed to be done to explain mechanism under hydrothermal conditions.

Relying upon our past experience we employed ethanol Water mixture 70:30 as a solvent. Ethanol coordinates with metal ions and its solution with water make hydrothermal conditions optimum for the preparation and growth of particles.

It has been observed that Chlorides when interact with hydroxyl ions behave markedly different from others. The KOH in the system will react with strontium chloride SrCl$_2$ in a double displacement reaction. The balanced equation for this reaction is given as:

$$2\text{KOH} + \text{SrCl}_2 \rightarrow \text{Sr(OH)}_2 + 2\text{KCl}$$  \hspace{1cm} (5)

Aggregation is observed for HNZF/SF system, where Sr is in contact with OH$^-$ ions. This aggregation can be attributed to larger ionic radius and surface free energy of Sr, leading to growth of particles. The ionic radii of Sr$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ are 0.132, 0.77 and 0.69 Å respectively. On subject to hydrothermal treatment, nucleation and growth of particles began which result into self-assembly, Ostwald ripening takes place [Ostwald 1897]. In NZF/SF, the thin nanowires have been formed, which is expected that there had been further splitting once they formed thick wires. The formation of thin wires is endorsed probably due to addition on one crystallographic plane by reason of steric hindrance on others.

Fig. 4.19 shows FTIR absorption spectra of Nanocomposites CNZF/SF and HNZF/SF prepared without surfactant via chemical combustion method and
hydrothermal method which was recorded in the range of 4000 – 400 cm\(^{-1}\). FTIR spectrum confirms the formation of Nano composite phase and also suggests presence of adsorbed moisture. Apart from characteristic bands other bands present are attributed to various stretching’s(C−O, C=C, C–H etc.).

Fig.4.20 shows the ferromagnetic behaviours of CNZF/SF and HNZF/SF ferrites by measuring M-H hysteresis at room temperature. It is observed that magnetic properties of these composite especially of nanowires are different. The hysteresis loops are two–step processes, typical of the exchange–spring regime. They show positive nucleation fields which is a peculiar prediction of a micro-magnetic model developed for perpendicular bilayers where the shape anisotropy contribution is also taken into account [Casoli et al. 2008].

The overlap between the recoil curves and the main loop shows that the demagnetization process was perfectly reversible from soft phase nucleation field down to the hard phase reversal field. In the low magnetizing field the Hc and Mr show the loop as rectangular shaped indicating the strong coupling between hard and soft phases leads to a magnetization reversal.

The dielectric constant (\(\varepsilon_r\)) and loss (\(\tan\delta\)) measurements in the frequency range of 100 Hz to 1 MHz is given in the Fig. 4.21. Again the observed behaviour of the dielectric dispersion can be explained on the basis of Koops theory [Koops et al. 1951] and Maxwell-Wagner interfacial type of polarization [Wagner et al. 1913]. As the frequency of the applied field is increased, the electrons reverse their direction of motion more often. This decreases the probability of electrons reaching the grain boundary and as a result the polarization decreases.

In the present case all the grains are of Nano size where the large surface boundaries and are the region of high resistance. This can reduce the interfacial polarization and hence improve the frequency dependent polarization process. A similar behaviour is involves in the case of loss factor. With the addition of Zn and Sr in NiFe\(_2\)O\(_4\) the dispersion in dielectric constant is observed up to frequency of 120 MHz.

It is reported in the literature that in 1D nanostructure, long range interaction is curtailed due to lack of periodicity and short range one is significantly modified near
the surface boundary. However, Eliseev et al. [2009] reported that the compressive stress induced by surface curvature would produce an effective tensile in the length direction of nanowires.

Theoretical deductions by first–principles calculation responsible for the surface compressive stress caused by 1D confinement produces an effective tensile in the length direction in nanowires and then leads to a big off-centre displacements that enhances the polarization.

5.5 Hydrothermal and chemical combustion synthesis of CNZF/BT and HNZF/BT:

5.5.1 Multiferroic, Magnetoelectric and optical properties of CNZF/BT and HNZF/B nanostructures:

XRD patterns of the nanostructures revealed the presence of both the spinel and perovskite phases, corresponding to NZF and BT respectively, prepared by both chemical combustion and hydrothermal routes as shown in Fig. 4.23. The reflections 001/100 and 200/002 are the splitting of cubic into tetragonal phase. The distortion ratio c/a of tetragonal phase is 1.007 and 1.0083, respectively, for CNZF/BT and HNZF/BT. The broadening of the full width at half maxima of the diffraction peaks indicates the formation of nanocrystalline products.

Fig. 4.24 reveals the TEM images at different magnification of CNZF/BT and HNZF/BT composite. From the morphological results it was found that the products consist of nanoparticles of very small size having cubic like faces of average diameter 4 nm in case of CNZF/BT and HNZF/BT composite showed the nanowires like structures consists of large number nanowires. Possible mechanism of their formation is explained as under:

In case of CNZF/BT, the chemical combustion method was used where the Nano fabrication temperature (annealing) is low (500 °C) results small growth of grains. Generally, nitrates serve an excellent provider of oxidising environment. While the urea and PEG serve as reducing and chelating agents. PEG and Urea gets chelation with metal ions. Formation of ammonium nitrate by the reaction of urea with metal nitrate ions helps in lowering of ignition temperature and provides
combustion at low temperature with ease. PEG too gets chelated with metal ions and help in combustion process.

As combustion takes place with flame release of gases like oxides of nitrogen, oxides of carbon dioxide and water along leads to shattering of material into Nano size product. HNZF/BT composite the fabrication of nanowires is achieved by hydrothermal synthesis using ethanol as solvent. This solvent plays key role to create various shapes because ethanol has such ability due to its high coordinating nature towards the metal cation. The main reason for the particles coarsening or Ostwald ripening process is the surface energy reduction [Ostwald et al. 1897].

This process involves formation of small crystalline nuclei in a suspension which is supersaturated and then it is followed by crystal growth, in which the bigger particles will grow at the cost of the smaller ones due to the energy difference between large particles and the smaller particles. The hydrothermal synthesis leads to particle coalescence if treated for longer period of hydrolysis temperature (180 °C for 48 h in the present case), due to an increased number of coalescence occasions. Addition of KOH helps in precipitation of material and provides basic environment for the reaction. The role of oriented attachment in hydrothermal conditions is that under dispersed conditions, the anisotropic particles are formed by successive collisions without grain rotation and can lead to various particle shapes.

The final particle can result from several attachment events along the same surface, giving an uncontrollable shape in agglomerates. It is believed that the present case is involves under dispersed conditions; the steric hindrance may have led to effective collisions in only one crystallographic direction due to different ionic radii of all metal ions resulting into formation of nanowires like structure [Verma et al. 2013].

Figures 4.25 & 4.26(a & b) shows the coexistence of ferromagnetism and ferroelectricity of CNZF/BT and HNZF/BT nanostructure by measuring magnetization versus magnetizing field (M-H) and polarization versus electric field (P-E) hysteresis curves at room temperature. The values of Pr for both of sample show improvement which is similar to the reported work of BT composites [Li et al. 2013; Majeed et al. 2013] are explained as: firstly; the surface defects by large value of surface to volume ratio of nanostructures. Secondly, the polycrystalline phase of
BT is tetragonal. This tetragonal phase with Nano grains has twin structure by which the stress resides near grain boundaries can easily control depolarization field and the long-range interactions support the development of homogeneous polarization; and the elastic constraints forms strain energetic and its stress relieving twinning mechanism. Therefore results in an enhancement of ferroelectric polarization [Frey and Payne 1996]. The third is the epitaxial strain growth between ferrite and ferroelectric interface introduced by the lattice mismatch between cubic of spinel (NZF) and tetragonal (BT) result in large ferroelectric polarization [Ederer and Spaldin 2005].

It has also observed that the NZF/BT composite prepared by hydrothermal synthesis observed higher value of polarization than by chemical combustion is explained on basis of shape of nanostructure. HNZF/BT composite has 1D nanowire like structure and the ferroelectric polarization in such type of nanowire system is explained on the basis of First-principles density functional theory using local density approximation Hellmann-Feynman theorem by Cai et al. [2009] for their ferroelectric system of perovskite PbTiO$_3$ nanowires. By assumption, the surface compressive stress caused by 1D shape produces an effective tensile in the length direction in nanowires and then leads to a big off-centre displacements that enhances the spontaneous polarization.

This enhancement in polarization is attributed to the competition between itself surface tension and near-surface depolarizing effect. Multiferroicity is the coexistence of ferroelectricity and ferromagnetism gives ME coupling whose strength is measured in terms of magnetoelectric coefficient (aE) under a static magnetic field Hdc, superimposed with a small ac magnetic field Hac. The aE is given by where t, is the sample thickness and Vout is the induced ME voltage. The variations of aE with Hdc at ac magnetic field frequency of 1093 Hz and ac magnetizing field of 5 Oe for both the composite of NZF/BT nanostructure at room temperature are shown in Figs. 4.25 & 4.26. Generally the value of aE is linearly increases to a maximum value and then deceases linearly to zero with varying Hdc of applied magnetic field.

But in the present case of NZF/BT, the aE is nonlinearly varying and also observe stability at certain value of applied Hdc magnetic field which depends on factors: Firstly; a MF contact consisting of a ferromagnetic layer (NZF) and a
ferroelectric (BT) means that NZF is responsible for spin waves as well as to avoid a decay of aE in long ferromagnetism, whereas the BT stabilizes the ferroelectric polarization is explained on the basis of Landau -Lifshits -Gilbert and Ginzburg -Landau dynamics of nonlinear response ME coefficient [Sukhov et al. 2013]. Secondly; the two-phase nanostructural composite coupled by interfacial strain where ME behaviour is strongly dependent on their Nano grains and the coupling interaction across the piezoelectric/magnetostrictive interface [Brosseau et al. 2010]. It is expected that a residual stress generated can be responsible for the eventual nucleation, evolution, and coalescence of voids which are strongly hinder the domain reorientation, and therefore control the resulting polarization of ME. Finally; the dependence of magnetoelectric yield on the bias field, Hdc may be ascribed to the nonlinear magneto stress coupling because it is believed that a bias field favours a parallel spin alignment for all magnetic domains so that the magnetostrictive response is more significant [Brosseau et al. 2010; Sukhov et al. 2013].

Fig.4.27 show the variation of dielectric constant ($\varepsilon_r$) and dielectric loss ($\tan\delta$) of CNZF/BT and HNZF/BT Nano composites measured at room temperature in the frequency range 20 Hz to 120 MHz. Both of the composites show variation in the dielectric constant in the low frequency region is explained on the basis of space charge polarization due to inhomogeneous dielectric structure. The inhomogeneities do exist due to impurities, porosity and grain structure. A slight decrease in $\varepsilon_r$ and $\tan\delta$ with the increase of frequency indicate dielectric dispersion follows the Maxwell-Wagner type interfacial polarization [Maxwell et al. 1973; Wagner et al. 1993].

Fig 4.28 shows fluorescence spectrum of NZF/BT Nano composites at room temperature. It is well known that the point defects, oxygen vacancies and interstitials are key factors responsible for emission spectrum. Composites prepared via hydrothermal synthesis as show remarkable high intensity of blue, green, yellow red and red band emissions than by combustion.