CHAPTER 7
DIELECTRIC STUDIES OF Ni AND Ba DOPED ZnO SAMPLES

In previous chapters, we studied the optical and magnetic properties of doped ZnO systems. Additionally, ZnO exhibits ferroelectric properties which can be exploited in various applications such as ferroelectric memories, nanogenerator, and nanooptoelectronics devices [241-243]. Thus ZnO is a unique a wide band gap semiconductor which exhibits ferromagnetic and ferroelectric properties with a predicted curie temperature above room temperature [47, 8]. There are several reports available in the literature on optical and magnetic properties of transition and non-transition metal doped ZnO [244-247], but still it is a good candidate for improving the ferroelectric properties which are of considerable significance in low dimensional ferroelectrics (FE) because of the demand for non-volatile FE memory and device miniaturization [248-250]. Generally, we use pervoskites for FE memory devices which are highly complicated and difficult to synthesize [251-253]. Real challenge is to achieve high remnant polarization, low coercive field and high Curie temperature for practical applications.

Under this scenario, ferroelectric and dielectric properties of doped ZnO systems are highly interesting for scientific research. In this chapter, we studied the following two series:

(i) Ni doped ZnO (Ni= 2%, 4% and 6%) samples prepared solid state route.
(ii) 5% Ba doped ZnO nanoparticles prepared by thermal decomposition method.

7.1 EFFECTS OF Ni DOPING ON STRUCTURAL, OPTICAL AND DIELECTRIC PROPERTIES OF ZnO

7.1.1 SYNTHESIS ROUTE

Ni doped ZnO samples were prepared by the conventional solid state reaction route. High purity zinc oxide (99.99% purity, Sigma Aldrich) and NiO (99.99% purity, Sigma Aldrich) were used as starting materials. To synthesize Zn$_{1-x}$Ni$_x$O (x=0.02, 0.04 and 0.06), appropriate amounts of starting chemicals were ground for 6 h in agate mortar. The powders were calcined at 600 °C for 12 h in air. Further, samples were ground again and compacted into pellets and sintered at 950 °C for 12 h.
7.1.2 STRUCTURAL ANALYSIS

7.1.2.1 X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction study is performed to investigate the effect of Ni doping on the crystal structure of ZnO. Reitveld refined XRD patterns of Zn$_{1-x}$Ni$_x$O (x=0.02, 0.04 and 0.06) samples sintered at 950º C are shown in figure 7.1.

![Reitveld refined XRD patterns of Zn$_{1-x}$Ni$_x$O](image)

**Figure 7.1:** Reitveld refined XRD patterns of Zn$_{1-x}$Ni$_x$O (inset shows the doping-induced peak shift).

The values of $\chi^2$ were in the range 1.7-2.5, which are good for estimations, as the profile fitting procedure adopted was minimizing $\chi^2$ functions. Rietveld profile refinement of XRD patterns demonstrates that all Bragg peaks are indexed in the wurtzite type hexagonal structure and there is no detectable peak from any other phase upto 4% of Ni but a few traces of NiO (111) phase were detected for x > 0.04 which shows that nickel content x > 0.04 is beyond the solid solubility limit of Ni in ZnO, part of Ni ions did not enter the crystalline structure of ZnO and crystallized alone forming NiO grains as indicated in the XRD pattern of 6% doped powder [254]. The refinement of the unit cell parameters (table 7.1) revealed that cell parameters slightly decreased with increase in Ni concentration, which can be assigned to a smaller ionic radius of Ni$^{2+}$ (0.55 Å) than that of the Zn$^{2+}$ (0.60 Å) and to the shifting of peaks to higher angles (shown in the inset of figure 7.1). Bond length shows the continuous decrease with
doping concentration. The average crystallite sizes vary from 31 to 48 nm which were estimated from the intense ZnO (101) reflection, using Scherrer’s relation. All the parameters calculated from the reteveld refinement are concluded in table 7.1.

Table 7.1: Calculated parameter from refinement.

<table>
<thead>
<tr>
<th>% Ni</th>
<th>Lattice Parameters</th>
<th>Bond length</th>
<th>R-factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a=b (Å) c (Å) V (Å)³</td>
<td>R_p R_wp R_exp χ² R_b R_f</td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>3.245 5.196 47.359</td>
<td>1.9741 7.9 12.7 9.45 1.7 3.7 2.2</td>
<td></td>
</tr>
<tr>
<td>4%</td>
<td>3.244 5.195 47.352</td>
<td>1.9740 7.7 13.4 9.26 2.08 3.4 2.12</td>
<td></td>
</tr>
<tr>
<td>6%</td>
<td>3.221 5.157 46.353</td>
<td>1.9602 13.9 21.2 13.6 2.5 5.15 2.9</td>
<td></td>
</tr>
</tbody>
</table>

7.1.2.2 FTIR STUDIES

The full scan transmittance spectra in the range 400-4000 cm⁻¹ are shown in the figure 7.2.

![FTIR Spectra](image)

**Figure 7.2:** The full range transmittance spectra of Zn_{1-x}Ni_{x}O. Inset (a) shows zoomed FTIR spectra in the range 400-600 cm⁻¹ and (b) shows the variation of IR bands corresponding with Ni content.

The low intensity absorption peaks observed around 3400, 2340 and 2925 cm⁻¹ are assigned to O-H vibration, CO₂ and C-H mode respectively. Absorption peaks at 1580 and 1415 cm⁻¹
correspond to the asymmetric $\nu_{as}$ (COO$^-$) and symmetric stretching $\nu_s$ (COO$^-$) vibrations of acetate species. The water molecule bending vibrational mode (H-O-H) appeared at 1640 cm$^{-1}$. The IR active characteristic broad band (optical phonon modes) of ZnO is observed in the spectral range 300-600 cm$^{-1}$.

The absorption bands are found to blue shift with Ni doping which shows the substitution of Ni atoms on Zn sites. The observed change in peak positions of ZnO absorption bands reflects that the Zn-O-Zn network is perturbed by the presence of Ni in its environment [255]. For the exact positions of Zn-O bands, IR band in the region 400-600 cm$^{-1}$ is shown in the inset (a) of figure 7.2 which is fitted by Gaussian and shows three bands $A_1$, $A_2$ and $A_3$. The band $A_1$ around 443 cm$^{-1}$ corresponds to the $E_1$ (TO) mode. The bands centered at 485 cm$^{-1}$ ($A_2$) and 533 cm$^{-1}$ ($A_3$) are surface phonon (SPM) modes and named as SPM [$A_1$ (TO)] and SPM [$E_1$(TO)], respectively. IR bands correspond to Zn shows a variation in vibrational frequencies with increase in the doping concentration of Ni, as shown in the inset (b) of figure 7.2. The shift in the band position on doping of Ni may be due the difference in ionic radii of Zn and Ni as well the structural changes induced due to the doping [256]. Calculated values of effective mass, force constant and bond length length of Zn(Ni)-O in Zn$_{1-x}$Ni$_x$O system are listed in table 7.2.

The effective mass of Zn (Ni)-O bond decreased with Ni substitution because of the lower atomic weight of Ni than Zn. Also, a decrease of the average force constant is observed with substitution of Ni which results an increment in the average Zn (Ni)–O bond length.

Table 7.2: The IR band and local structure data of Zn Ni-O bonds of Zn$_{1-x}$Ni$_x$O.

<table>
<thead>
<tr>
<th>Samples (Zn$_{1-x}$Ni$_x$O)</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Effective mass (atomic weight)</th>
<th>Force constant (N m$^{-1}$)</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x=0.02</td>
<td>443</td>
<td>12.8426</td>
<td>148.66</td>
<td>2.52</td>
</tr>
<tr>
<td>x=0.04</td>
<td>446</td>
<td>12.8374</td>
<td>150.62</td>
<td>2.24</td>
</tr>
<tr>
<td>x=0.06</td>
<td>452</td>
<td>12.8322</td>
<td>154.63</td>
<td>2.22</td>
</tr>
</tbody>
</table>
7.1.3 OPTICAL PROPERTIES

7.1.3.1 UV-VISIBLE STUDIES

To study electronic interactions near the band gap region due to doping of Ni, UV–Vis absorbance measurements were undertaken. The change in absorption peak due to doping indicates a change in the band structure. It is observed that absorption edges of Zn$_{1-x}$Ni$_x$O are at 372, 369 and 367 nm for x= 0.02, 0.04 and 0.06 respectively as shown in figure 7.3. The position of the absorption edge is observed to shift towards lower wavelength side with increase in Ni concentration in ZnO, indicating an increase in the band gap with Ni doping. This blueshift behavior can in principle be explained by the Moss-Burstein band filling effect, which is frequently observed in n-type semiconductors.

![Absorption spectra](image)

**Figure 7.3:** Absorption spectra of Zn$_{1-x}$Ni$_x$O for (a) x=2%. (b) x=4%. (c) x=6%. (d) Shows the variation of band edge with Ni doping.

7.1.3.2 PHOTOLUMINESCENCE STUDIES

To understand the behaviour of surface defects such as oxygen vacancies, room temperature PL emission spectra were recorded at an excitation wavelength of 325 nm which are shown in figure 7.4. A strong emission band appeared in ultraviolet region at around 390 nm (A) due to the recombination of free excitons and is generally assigned as near band edge (NBE) emission band [214].
This NBE peak is found to shift from 392 to 388 nm with increase in doping concentration of Ni. A low intensity broad band with multiple subpeaks (B, C, and D) in the visible emission region spanning the range from green to red is observed (figure 7.4). A variety of deep-level defects have been proposed as possible contributors to the emission in the visible regime. The blue emission peak (B) around 423 nm is probably due to two defect levels, either transition from Zn\text{ii} to valence band or transition from the bottom of the conduction band (CB) to interstitial oxygen (O\text{i}) level. The green light (C) emission centered at around 494 nm can be attributed to an oxygen vacancy (V\text{O}) and the emission feature at 520 nm (D) to antisite oxide (O\text{Zn}) [257, 258].

### 7.1.3 DIELECTRIC PROPERTIES

The temperature and frequency dependent dielectric constants are shown in figure 7.5. The inset of figure 7.5 shows the loss tangent behaviour. As shown in the figure, the dielectric constant and loss are strongly temperature and frequency dependent. At room temperature, the value of the dielectric constant is very high and it decreased for high frequencies. The shape of the dielectric curve at the transition temperature is highly asymmetric consisting of a long tail in the lower temperature region and a sharp decrease after transition temperature. The dielectric anomaly around 320°C was observed to shift towards lower temperature with
increasing doping concentration, which is higher than earlier reported values [259] and may be beneficial for the application point of view.

The transition may be ferroelectric phase transition attributed to both order disorder characteristic (weather interaction in direct or phonon mediated between off centered Ni ions) and displacive characteristic (relative translational shift of Zn and O sublattices). The origin of the possible ferroelectric phase transition could be explained on the basis of the ionic radii difference between the Zn$^{2+}$ and the dopant ions Ni$^{2+}$. Due to which Ni$^{2+}$ can occupy the off centered position, leading to permanent local electric dipoles and thereby introducing dielectric behavior. Another aspect for the dielectric behavior is the oxygen vacancies. The large value of dielectric constant for all samples at transition point, is probably extrinsic due to the space charge formation. The dielectric behavior is still not very clear in this system further investigations are needed to predict the mechanism behind it.

**Figure 7.5:** Dielectric dispersion of Zn$_{1-x}$Ni$_x$O ceramics, (a) x=0.02, (b) x=0.04 and (c) x=0.06, as a function of temperature. Inset shows the loss for the corresponding composition.
7.2 HIGH T\textsubscript{C} FERROELECTRICITY IN Ba-DOPED ZnO NANOPARTICLES

7.2.1 SYNTHESIS ROUTE

Ba doped ZnO nanoparticles were synthesized by the thermal decomposition method by using chemicals of analytical grade. Initially, 0.16 mol C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O (oxalic acid) was dissolved in 100 ml of deionised (DI) water with vigorous stirring. Then, 0.02 mol diethanolamine (DEA) is added to get homogenous DEA/C\textsubscript{2}H\textsubscript{2}O\textsubscript{4}·2H\textsubscript{2}O solution (A). Now, 0.02 mol zinc nitrate was dissolved in 100 ml of DI water in which appropriate amount of barium nitrate (5\%) was added to get the solution B. Finally, B was added drop wise in the aqueous solution A. White precipitates were formed and the suspension was continuously stirred at room temperature and kept for 12h to settle down. Then, precipitates were filtered, washed with DI water and ethanol water several times, dried at room temperature and calcined at 500°C for 2h.

7.2.2 STRUCTURAL CHARACTERIZATION

7.2.2.1 X-RAY DIFFRACTION ANALYSIS:

Rietveld refined XRD patterns of pure and Ba doped ZnO nanoparticles are shown in figure 7.6 in which all Bragg peaks are indexed in the wurtzite type hexagonal structure with space group P63mc. No indications of any secondary phases or clusters were observed, confirming the single phase of samples.

It also confirms that Ba doping has not altered the basic wurtzite crystal structure of samples. It can be seen from the figure 7.6 that observed and calculated values were perfectly matching. Calculated refined parameters such as R\textsubscript{p} (profile fitting R-value), R\textsubscript{wp} (weighted profile R-value) and χ\textsuperscript{2} (goodness-of-fit quality factor) obtained after the final cycle of refinement are summarized in Table 7.3.
Figure 7.6: Reitveld refined XRD patterns of pure and Ba doped ZnO nanoparticles.

Low values of $\chi^2$ and profile parameters ($R_p$ and $R_{wp}$) suggest the good quality of samples and effectiveness of refinement. Lattice parameters slightly increased after Ba doping, which can be assigned to a bigger ionic radius of $\text{Ba}^{2+}$ than that of the $\text{Zn}^{2+}$, which shows the incorporation of Ba ions on Zn sites. Average crystallite sizes determined by Scherrer’s formula was found to be 29 nm for pure ZnO and 25 nm for Ba doped ZnO sample, which is dependent on the increasing broadening of peaks with doping.

Table 7.3: Calculated parameters from refinement.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Lattice Parameters</th>
<th>Bond length (Å)</th>
<th>R-factors</th>
<th>R-factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a=b (Å)</td>
<td>c (Å)</td>
<td>V (Å$^3$)</td>
<td>$R_p$</td>
</tr>
<tr>
<td>Pure ZnO</td>
<td>3.248</td>
<td>5.208</td>
<td>47.604</td>
<td>1.977</td>
</tr>
<tr>
<td>5%-%Ba</td>
<td>3.249</td>
<td>5.211</td>
<td>47.642</td>
<td>1.979</td>
</tr>
</tbody>
</table>
7.2.2.2 SEM ANALYSIS

Microstructures of pure and Ba doped ZnO samples, investigated by FESEM are shown in figure 7.7, which show that the pure ZnO nanoparticles sample has a smooth surface with porous network (figure 7.7a), due to the effect of surfactant (DEA) used in the synthesis process but the grains are equally distributed in size and shape. FESEM image of pure ZnO shows the spherical shaped nanoparticles of small average grain size (80-100 nm). While, after Ba doping, small spherical grains are transformed to small cubes and rods with increased porosity (Figure 7.7 b & c).

![FESEM images of pure and Ba doped ZnO samples](image)

**Figure 7.7:** FESEM image of (a) pure and (b, c) 5% Ba doped ZnO with different resolutions.

7.2.2.3 FTIR STUDIES

Figure 7.8a shows FTIR transmittance spectra of Zn$_{1-x}$Ba$_x$O (x=0, 0.05) nanoparticles at room temperature in the range 400-4000 cm$^{-1}$ which encompass several important stretch modes involving hydrogen bonded to carbon as well as to oxygen and ZnO bonding. An absorption band revealing vibrational properties of ZnO is observed for both samples in the range 400–
600 cm\(^{-1}\). Common bands, such as the broad O-H band centred around 3420 cm\(^{-1}\) and the 1640 cm\(^{-1}\) H\(_2\)O vibrational band were observed due to high surface area of these materials resulted in rapid adsorption of water from the atmosphere. Two Peaks of very weak intensities at 2920 and 2960 cm\(^{-1}\) due to C–H stretching vibrations of alkane groups were also observed. These specific peaks correlate well with the observed frequencies of the C–H\(_2\) asymmetric stretch (~2926 cm\(^{-1}\)) and C–H\(_3\) asymmetric stretch (2962 cm\(^{-1}\)) of saturated hydrocarbons, respectively [260, 261]. The absorption at 2370 cm\(^{-1}\) is because of the presence of CO\(_2\) molecules in air.

Figure 7.8: Full range transmittance spectra (b) Zoomed spectra fitted with Gaussian for pure and Ba doped ZnO.

The IR active characteristic broad band (optical phonon modes) of ZnO is observed in the spectral range 400-600 cm\(^{-1}\). It can be seen that intensity of the ZnO bond decreased after doping of Ba; an evidence of good crystalline quality of undoped ZnO samples. For the exact positions of the Zn-O bands, the zoomed spectra in the range 400-600 cm\(^{-1}\) are shown in figure 7.8b, fitted by Gaussian showing three bands A\(_1\), A\(_2\) and A\(_3\). According to the literature [262], the band A\(_1\) around 436 cm\(^{-1}\) is corresponding to the E\(_1\)(TO) mode. The bands centred at 487 cm\(^{-1}\) (A\(_2\)) and 535 cm\(^{-1}\) (A\(_3\)) are surface phonon (SPM) modes and named as SPM [A\(_1\)(TO)] and SPM [E\(_1\)(TO)] respectively. The IR bands corresponding to Zn show a
variation in the vibrational frequencies after Ba doping which may be due to the difference in ionic radii of Zn and Ba as well the structural changes induced due to doping [263].

### 7.2.3 OPTICAL PROPERTIES

#### 7.2.3.1 UV-VISIBLE STUDIES

For the realization of ZnO based optical devices, band gap tuning is a prerequisite. Room temperature optical absorption spectra of pure and Ba doped ZnO nanoparticles studied by UV-visible spectroscopy in the range 300-800 nm are shown in figure 7.9. A sharp absorption edge at around 375 nm, a characteristic of ZnO, is observed in both samples. With the effect of Ba doping, it is observed that position of the absorption edge shifts towards higher wavelength side, indicating a decrease in the band gap with Ba doping.

![Figure 7.9: Absorption spectra of pure and Ba doped ZnO. Insets show Tauc plots of samples.](image-url)
Chapter-7

Band gap of samples were estimated by extrapolation of linear portion of \((\alpha h \nu)^2\) versus \(h \nu\) curve (inset of figure 7.9) by using the Tauc plot relation \(\alpha \propto (h \nu - E_g)^{1/2}\) for direct band gap semiconductors between the absorption coefficient (\(\alpha\)) and the energy band gap (\(E_g\)), where \(h\) is the Planks constant and \(\nu\) is the frequency of incident photon. Band gaps are observed to be 3.18 eV for pure and 3.14 eV for Ba doped ZnO, respectively. This optical energy band gap contraction and the absorption edge red shift with 5% Ba doping may be attributed to the sp–d spin-exchange interactions between band electrons and the localized d electrons of the Ba ion substituting the cation. The s–d and p–d exchange interactions might have given negative and a positive correction to the conduction- and valence-band edges, respectively, resulting to the band-gap narrowing [264].

7.2.3.2 PHOTOLUMINESCENCE STUDIES

Figure 7.10a shows the room temperature PL spectra for pure and Ba doped ZnO nanoparticles, which were taken by using an excitation wavelength of 325 nm. Both samples have shown two emission bands; one sharp emission in the UV region, corresponding to the near band edge (NBE) emission which is related to the recombination of free excitons between conduction and valence bands and other broad deep level emission in the visible region caused by impurities and structural defects which is only observed in Ba doped ZnO samples. Red shift in the NBE emission (around 390 nm) similar to shift in absorption edge in emission spectra was observed.

Figure 7.10b shows the broad emission band fitted with Gaussian corresponding to defect states for Ba doped ZnO sample. It is observed that defect states appear with Ba doping which can be understood by considering the Ba incorporation process in nanoparticles. \(\text{Ba}^{2+}\) ions can incorporate into the ZnO nanostructures in two different ways either creating oxygen vacancies or incorporating as interstitials, while pure ZnO nanoparticles have good crystal quality without any defect and oxygen vacancies, which may cause the appearance of sharper and stronger UV emission and a suppressed and weakened blue and green emission in comparison to pure ZnO nanoparticles.
Blue emission peaks at around 454 and 479 nm may be assigned to the energy of transition of electron from interstitial Zn (Zn$_i$) to Zn vacancies (V$_{Zn}$) and to the transition between the oxygen vacancy and interstitial oxygen (O$_i$), respectively and the emission peak observed at 422 nm can be attributed to the energy of transition of electron from the bottom of conduction band to the O$_i$ level. The green emission peak (~505 nm) could be due to the transition from Zn$_i$ levels to O$_i$. The debatable emission around 524 nm may be due to several type of defects such as V$_{O}$ (oxygen vacancies), Zn$_i$, V$_{Zn}$ and O$_i$. Thus, it can be concluded that the Ba-doping leads to red shift in NBE and increase in intrinsic defects such as V$_{O}$ and O$_{Zn}$ density.

7.2.4 DIELECTRIC PROPERTIES

Dielectric constant ($\varepsilon_r$) for Ba doped ZnO sample has been found to decrease with increasing frequency in the frequency range of the measurement (figure 7.11a). Dispersion in $\varepsilon_r$ has been found to be maximum in the low frequency region for Ba doped ZnO nanoparticles at all temperatures and at high frequencies, it is almost independent of frequency as all type of polarisations contribute at low frequency region while at high frequency, only electronic polarisation sustains.
The strong dependency of dielectric constant and loss for Ba doped ZnO with frequency and temperature are shown in the figure 7.11b.

**Figure 7.11:** (a) Variation of dielectric constant with frequency. (b) Variation of dielectric constant with temperature. (c) Variation of ac conductivity with frequency. (d) Variation of ac conductivity with temperature.

The observed large value of the dielectric constant at room temperature could be explained due to the behaviour of nanoparticles as nanodipoles under the application of an electric field i.e. as the particle size is small, the number of particles per unit volume is very large, resulting in an increase in the dipole moment per unit volume and hence to a high dielectric constant or it may be due to the space charge formation. The shape of the dielectric curve at the transition temperature is highly asymmetric consisting of a long tail in the lower temperature region and a sharp decrease after transition temperature 330°C, which is higher than earlier reported values in doped ZnO [259] and may be beneficial for the high temperature ferroelectric applications. The transition may be ferroelectric phase transition attributed to both order disorder characteristic and displacive characteristic (relative
translational shift of Zn and O sublattices) or due to the structural modification induced by Ba dopant in ZnO, which greatly affects the electronic and dielectric properties.

Figure 7.11 (c and d) show the frequency and temperature dependence of ac conductivity ($\sigma_{ac}$) for Ba doped ZnO sample, which was calculated using the formula as follows:

$$\sigma = 2\pi f \tan \delta \varepsilon \varepsilon_0$$

where, $f$ is the applied frequency, $\tan \delta$ is the dielectric loss, and $\varepsilon$ and $\varepsilon_0$ are the dielectric permittivity of free space and the sample, respectively. An increase in conductivity with frequency was observed. The probable ferroelectric to paraelectric phase transition was observed at 330°C supporting the transition in dielectric measurements.

7.2.5 FERROELECTRIC PROPERTIES

Polarization-electric field (P-E) curve for 5% Ba doped ZnO sample is shown in figure 7.12, which confirms the ferroelectric nature of the sample.

![Polarization-electric field (P-E) curve for 5% Ba doped ZnO sample.](image)

**Figure 7.12:** Hysteresis curve of Ba-doped ZnO nanoparticles.

The remnant polarization and coercive field were measured to be 1.01 $\mu$C/cm$^2$ and 2.02 kV/cm$^{-1}$ respectively. However, pure ZnO nanoparticles did not show hysteresis. The origin of the possible ferroelectric phase transition could be explained on the basis of the
ionic radii difference of Zn$^{2+}$ and dopant ions Ba$^{2+}$. Thus, Ba$^{2+}$ cannot occupy the position of Zn$^{2+}$ which creates the lattice mismatch, leading to permanent local electric dipoles and thereby introducing ferroelectric behaviour. Another aspect for the ferroelectric phase transition is the oxygen vacancy which is strongly supported by PL spectra. The role of oxygen vacancy is more important in determining degree of coupling between dipoles and in forming the long range or short range ordering. The dielectric behaviour is still not very clear in this system and further investigations are needed to predict the mechanism behind it.

7.3 CONCLUSIONS:

In summary, with a motive to study doping induced ferroelectric properties, ZnO nanoparticles with Ni and Ba doping were successfully synthesized. Both the series of samples followed the wurtize structure of ZnO, small peak corresponds to NiO phase appears in 6% Ni doped ZnO sample. FESEM images of Ba doped nanoparticles show change in the structure of nanoparticles after Ba doping. FTIR spectroscopic measurements show a broad band in the range 400-600 cm$^{-1}$ corresponding to ZnO. Red shift in band gap and enhanced defect states after Ba doping were also observed beside that with increase in doping concentration blue shift is observed in Ni doped ZnO samples. In dielectric studies, high value of dielectric constant and transition temperature (~ 330°C) were observed in all the samples. Ferroelectric behavior is only observed in Ba doped ZnO nanoparticles. This shows the high temperature ferroelectricity with high value of remnant polarization (1.01 μCcm$^{-2}$) and low coercive field (2.02 kVcm$^{-1}$) may play an important role in the miniaturization of devices and make it potential candidate for nano-optoelectronics, nanostorage and nanoscale memory devices.