Chapter 7

Dielectric Properties of NiO Nanoparticles

7.1 Introduction

Science and technology of nanomaterials has recently witnessed much progress in the synthesis and applications of nanomaterials [290–294]. Among them, nickel oxide (NiO) nanostructures have been studied extensively due to their exceptional optical, electronic, magnetic, thermal, mechanical and catalytic properties. For instance, a better performance of nanocrystalline thin film coated heterojunction organic photovoltaic cells is observed due to increase in the open circuit voltage. This is on account of favorable energy band levels, interface passivation, p-type character, crystallinity, smooth surface, and optical transparency [295]. Bulk NiO is an antiferromagnetic insulator with Neel temperature of 523 K [296]. Instead, NiO nanostructures are paramagnetic and their improved antioxidant property is useful for biosystems applications.
Further corrosion and wear resistance of mild steel is increased by using NiO based nanocomposite coatings [298]. The superior catalytic activity of NiO nanocrystals which depends on their size and morphology, find applications in batteries and fuel cells [299], chemical synthesis [300] and electrochemical based sensors [301]. In addition, a range of NiO based electrochemical sensors are developed to identify biological compounds like H₂O₂ [302], glucose [303], methanol [304], amoxicillin [305], and insulin [306]. Besides, reports reveal that NiOₓ can serve as p-type channels in transistors. The electrical performance of nickel oxide films can improved by controlling the stoichiometry defects which alters its electronic structure. Further, reports too confirm that physical, chemical, electrical and dielectric properties of nanostructures synthesized through chemical methods can be modified by suitable choice of precursor [52], solvent type [307], surfactants [54], precipitating agent [56, 146], doping [308–310], processing condition [53, 153] and calcination temperature [55]. This can cause a significant change in the microstructure of nanostructures which strongly influence their physical and chemical properties. Further, the nature of surfactants used for the synthesis of nanomaterials by bottom-up technique can tailor their properties by reducing the surface energy and preventing the agglomeration between the nanoparticles through either steric hindrance or repulsive electrostatic forces [299, 311]. Recently we have investigated the role of surfactant and mineralizer type on phase stabilization of un-doped zirconia nanocrystals produced by chemical precipitation [56, 146]. Although studies pertaining to electrical and dielectric properties of NiO nanocrystals have been reported, the influence of surfactant type on these properties is not well understood. In this context, the influence of
neutral polymeric (polyvinylpyrrolidone (PVP)) and (cationic cetyl trimethyl ammonium bromide (CTAB)) surfactant on electrical and dielectric properties of NiO nanocrystals synthesized through chemical precipitation method is explained in this chapter.

### 7.2 Experimental Methods

#### 7.2.1 Synthesis of NiO nanoparticles

NiO nanocrystals were synthesized by arrested chemical precipitation method. The reagents used for synthesis are NiCl$_2$.6H$_2$O (precursor), PVP/CTAB (surfactant), and NH$_4$OH (mineralizer). The surfactant (1.5 g) is added to 60 ml of distilled water taken in a 500 ml beaker and stirred for 10 minutes. Then 8.7 g of NiCl$_2$.6H$_2$O is added to the solution and the resulting mixture is stirred for two hours at room temperature. Finally, metal hydroxide is precipitated by adding alkaline mineralizer NH$_4$OH (0.5 M) drop by drop till pH of the solution is ~ 9.3. The solution is stirred continuously for 30 minutes. The suspension containing green precipitate is then centrifuged using deionized water for removing the surfactant. Finally the precipitate in centrifuged with ethanol for three times. The obtained nickel hydroxide is dried at 50 °C for 36 h and on calcination at 300 °C NiO nanocrystals are formed. The as-prepared samples obtained using surfactants PVP and CTAB are labeled as A and B respectively.
7.2.2 Characterization techniques

The samples are characterized using X-Ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), Fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy, UV-Visible absorption spectroscopy and photoluminescence (PL) spectroscopy techniques. The specifications of X-Ray diffractometer, high resolution transmission electron microscope, photoluminescence spectrometer and micro-Raman spectrometer are given in Chapter 3 and that of Fourier transform infrared spectrometer is given in Chapter 4. The UV visible absorption spectra of the NiO samples dispersed in ethanol were recorded at room temperature in the wavelength range of 200-700 nm using Varian CARY-100 UV-Vis spectrophotometer. In order to analyze dielectric properties the as-prepared samples were made into green pellets of 1 cm diameter with 0.18 cm thick. The dielectric response of samples was measured using HIOKI 3532LCR HITESTER instrument in the frequency range of 42 Hz - 4 MHz.

7.3 Results

7.3.1 X-Ray diffraction analysis

X-ray diffractograms of samples A and B are depicted in Fig. 7.1. The diffraction peaks (at 300 °C) are compared with JCPDS card No. 47-1049 (space group, f\text{m}3\text{m}(225)). The samples showed characteristic diffraction peaks of face centered cubic phase at 2\theta values 36.9, 43, 63.1, 75 and 79.4 degrees from lattice planes (111), (200), (220), (311) and (222) respectively. The average
grain size of samples is determined using Scherer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta},$$  \hspace{1cm} (7.1)

where $D$ is the grain size, $\beta$ is the broadening of diffraction peak estimated at half of its maximum intensity (in radians), $\theta$ is the Bragg angle (in degrees) and $\lambda$ is the wavelength of Cu K\textalpha\ radiation (1.5406 Å). The average grain size of both the samples calculated from the most intense peaks is about 8 nm. The lattice parameters such as distance between adjacent planes ($d$), lattice constant ($a$) and volume of unit cell are calculated from X-ray diffractogram. The volume of unit cell of sample B is slightly larger than that of A.

Figure 7.1: X-ray diffractogram of NiO samples A and B
### 7.3.2 Microstrain analysis

**Williamson-Hall method**

Microstrain is a measure of lattice dislocation which is due to crystal imperfections. The strain in as-prepared nanocrystals is estimated from the XRD line profile using integral breadth analysis [312]. In this analysis, the broadening ($\beta_{\text{size}}$) due to small crystallite size is described by Scherer equation ($K\lambda/D\cos\theta$). The microstrain broadening $\beta_{\epsilon}$ is approximated by Gaussian function as $4\epsilon\tan\theta$. Hence, broadening due to both size and strain can be expressed as:

$$\beta^2 = \left( \frac{k\lambda}{D\cos\theta} \right)^2 + 16\epsilon^2 \tan^2\theta,$$

(7.2)

![W-H-plots, (a) NiO samples A and (b) B](image)

Figure 7.2: W-H-plots, (a) NiO samples A and (b) B

The above equation can be expressed in the form of W-H equation as:

$$\beta^2 \cos^2 \theta = \left( \frac{k\lambda}{D} \right)^2 + 16\epsilon^2 \sin^2 \theta,$$

(7.3)

where $\beta$ is the integral width of XRD line in radians, $\theta$ is the position of peak, $K$ is a constant, $\lambda$ is the wavelength of CuK$\alpha$ radiation (1.5405 Å), $D$ is the
average crystallite size and $\varepsilon$ is the microstrain. The average grain size and microstrain of samples A and B are estimated by plotting $\beta^2 \cos^2 \theta$ versus $16 \sin^2 \theta$. From the linear fit of data (Fig. 7.2), microstrain can be estimated from slope and average crystallite size from y-intercept. The microstrain is compressive and attributed to lattice shrinkage during nucleation of nanocrystals [313][31].

### 7.3.3 Transmission electron microscopy analysis

Transmission electron microscopy (TEM) images of nickel oxide samples A and B reveal the presence of nanorods and nanoparticles (Figs. 7.3 and 7.4). The shape of nanoparticles appears to be square and rectangle. The size of nanoparticles and nanorods varies between $\sim$ 3 to 7 nm. The maximum length of nanorods is found to be around 27 nm. The selected area diffraction pattern of samples shows that the nanoparticles are polycrystalline in nature. The lattice fringes (Figs. 7.3b and 7.4b) observed with high resolution images of both samples are separated by 0.22, 0.29 and 0.25 nm which corresponds to d-spacing of (200), (220) and (111) planes of cubic NiO (JCPDS: 47-1049, 89-5881).

![HRTEM images of NiO sample A](image)

*Figure 7.3: HRTEM images of NiO sample A, a) Low magnification b) High magnification and c) SAED pattern*
7.3.4 UV-Visible absorption spectroscopy

UV visible absorption spectra of NiO samples A and B are presented in Fig. 7.5. Both samples show prominent absorption peaks at $\sim 280$ and $\sim 260$ nm respectively. The direct band gap energy of nanocrystals can be estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$. The optical band gaps are obtained by extrapolating the linear portion of plot to intercept photon energy axis as shown in Fig. 7.5. The estimated $E_g$ values of samples are found to be $\sim 3.6$ eV. The red shift observed is due to surface defects which give raise to near band edge-emission [314].

Figure 7.5: UV-visible absorption spectra, a) NiO samples A and b) B, (inset shows band gap determination)
7.3.5 Photoluminescence spectroscopy analysis

Photoluminescence (PL) spectra of samples yield information about nature of defects present in nanocrystals. The point defects of metal oxide nanoparticles are generated due to interstitial/vacancy of metal and oxygen ions. These defects are associated with new energy levels in the band gap region which gives rise to near band edge and deep level defect emissions. The PL spectra of samples A and B for an excitation wavelength of 250 nm is presented in Fig. 7.6. The spectrum is analyzed with multiple Gaussian curves by deconvolution. The spectrum of sample A is fitted with peaks at 406 nm (3.06 eV), 429 nm (2.89 eV), and 438 nm (2.83 eV), while sample B at 319 nm (3.9 eV), 359 nm (3.45 eV), 382 nm (3.24 eV), 406 nm (3.06 eV), 429 nm (2.89 eV) and 456 nm (2.72 eV). The near band edge UV emissions are attributed to 3d⁸⁻3d⁸ electronic transitions of Ni²⁺ ions, while violet and blue emissions are due to radiative transition of electrons from interstitial shallow donor levels (Ni²⁺) created by oxygen vacancies to the valence band [315].

7.3.6 Fourier transform infrared spectroscopy analysis

The presence of structurally bonded hydroxyl groups on surface of NiO samples can be detected from their respective FTIR spectra (Fig. 7.7). Both samples exhibited broad vibrational band at 3420 cm⁻¹ ascribed to O-H stretching vibration of structurally bonded hydroxyl group formed at defect sites [316]. The intensity of vibrational band at ~ 3420 cm⁻¹ is higher in B which confirms the presence of more surface hydroxyl groups and hence the surface defects. Further, the samples also exhibits vibrational band at 1620 cm⁻¹ attributed to
H-OH bending vibration of molecular water adsorbed on surface. The Ni-O vibrational band of samples A and B are at ∼ 421 and ∼ 409 cm\(^{-1}\) respectively [317]. Besides, the two bands at 1300-1460 cm\(^{-1}\) and 2800-3000 cm\(^{-1}\) of samples A and B are ascribed to inherently adsorbed organic compounds and stretching vibration of C-H bond respectively.

### 7.3.7 Micro-Raman spectroscopy analysis

The microstructural details of nickel oxide samples is further confirmed from their micro-Raman spectra (Fig. 7.8) [318]. Sample A exhibited one-phonon transverse optical band (TO) at 478 cm\(^{-1}\) and 2 longitudinal optical mode (LO) 1055 cm\(^{-1}\) [319]. But NiO sample B showed vibrational band attributed to two-phonon modes (2TO) at 682 cm\(^{-1}\) and 2LO band at 1049 cm\(^{-1}\). Further, sample B also shows a band at ∼ 507 cm\(^{-1}\) attributed to a one-phonon plus one-magnon vibration. This band originates due to strong phonon-magnon
interaction at defect sites [320]. Besides, peaks at 215 cm$^{-1}$ and 354 cm$^{-1}$ of sample B are due to high concentration of nickel ion vacancy [318].

**Figure 7.8: Raman spectra of the NiO samples**

### 7.3.8 Impedance spectral analysis

The electrical properties of samples were analyzed from their impedance spectra. The spectra are obtained by plotting imaginary part of impedance $Z''$ versus real part $Z'$ which represents the Cole-Cole (semicircle) plot (Fig. 7.9).

Figure 7.7: FTIR spectra of the NiO samples
Figure 7.9: Complex impedance spectra of the NiO samples A and B at room temperature

The plot shows a depression at centre due to non-Debye relaxation of ions [321]. The electrical properties of NiO samples are represented at higher frequency side of impedance spectra by a parallel combination of bulk resistance $R_b$ and bulk capacitance $C_p$. From the intersection of semicircle at higher frequency side of $Z'$ axis, $R_b$ values of samples A and B are found as $\sim 6.5$ and $\sim 12$ k Ohm respectively. The $C_p$ values are estimated using the relation $\omega_{\text{max}} R_b C_p = 1$, where $\omega_{\text{max}}$ is the angular frequency at maxima of semicircle. The expected $C_p$ values of samples A and B are $\sim 62.16$ and $\sim 44.2$ pF respectively. Since the capacitance values are of the order of picofarad, conduction is mainly through bulk of the material [322]. The frequency dependence of real ($Z'$) and imaginary ($Z''$) parts of impedance spectrum is shown in Fig. 7.10.
7.3.9 Dielectric spectral analysis

The frequency dependence of dielectric properties of samples is studied by estimating the relative permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ using the relations:

\[ \varepsilon' = \frac{Cd}{A\varepsilon_0}, \]  
\[ \varepsilon' = \varepsilon'' \tan\delta, \]  

where $C$ is the capacitance and $\tan\delta$ is the loss tangent. The frequency dependence of $\varepsilon'$ and $\varepsilon''$ of samples are in the frequency range of 42 to 4 MHz as shown in Fig. 7.11. The hopping frequency of charge carriers is analyzed by plotting $(\tan\delta)$ as a function of angular frequency (log $\omega$) (Fig. 7.12).
Figure 7.11: Variation of dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) with frequency

Figure 7.12: Variation of $\tan\delta$ with frequency
7.4 Discussion

In the present study, NiO nanocrystals were obtained through calcination of metal hydroxides synthesized by surfactant assisted chemical precipitation method. On dissolving the metallic salt in aqueous solution of surfactant (CTAB/PVP), polar head groups get attached to the surface of metallic ions and forms a nanocage which stabilizes the ions against agglomeration. Moreover, the hydrolysis of metallic ions takes place inside the nanocage. Hence stabilizing effect of surfactants determines the hydrolysis (nucleation) rate of metallic ions and the growth of metal hydroxides along preferred directions. Higher stabilization of metallic ions against agglomeration leads to slower hydrolysis rate. This reduces the likelihood formation of metal hydroxides with un-coordinated metallic/oxygen ions than rapid hydrolysis.

The stabilization mechanism and thereby hydrolysis rate depends on type of surfactant used for synthesis. PVP stabilizes the metallic ions by steric and electrostatic stabilizations. The nitrogen atom of amide group gives rise to steric stabilization by forming strong bond with metallic ions. At the same time the repulsive force between polyvinyl groups prevents the agglomeration of metallic ions through electrostatic stabilization. However, in CTAB the hydrophilic end (CH$_3$)$_3$-N$^+$ gets adsorbed on to the surface of metallic ions and forms a nanocage with its long alkyl hydrophobic chain pointing outwards (electrostatic stabilization). The stabilizing effect of PVP is higher than that of CTAB because of the strong bond formed by nitrogen atom with metallic ions. Consequently, hydrolysis rate of metal hydroxides in PVP assisted synthesis are slower than that of CTAB. The difference in hydrolysis rate determines
the microstrain of as-synthesized metal hydroxides. In the present case, W-H analysis reveals that, microstrain is compressive in both NiO samples A and B (Fig. 7.2). However sample A shows slightly higher compressive strain than B which causes a difference in their intrinsic defect levels as observed in PL spectra. Fig. 7.6 shows that sample B has high density of point defects (Ni$^{2+}$) than A. The unit cell volume calculated from prominent peaks of XRD spectra is higher for B. This is attributed to high concentration of Ni$^{2+}$ vacancies [323].

Investigations reveals that in nanostructured NiO the nature of point defects determine their electrical [324] and dielectric properties [325]. NiO is classified as 'Mott-Hubbard Insulator' [324, 326] due to its very low conductivity of the order of $10^{-13} \text{Ω}^{-1}\text{cm}^{-1}$ at room temperature [255, 326–332]. The conductivity of undoped NiO can be increased by introducing Ni$^{2+}$ ions in the lattice which causes the transformation of two adjacent Ni$^{2+}$ ions into Ni$^{3+}$ ions for acquiring charge neutrality. This transformation induces local lattice distortion and results in the formation of stable quadrupole complex consisting of one Ni$^{2+}$ vacancy and two adjacent Ni$^{3+}$ ions [328]. Besides, each Ni$^{2+}$ vacancy is associated with long range potential well which influence the localization of energy within the surrounding lattice of few atomic spacing [255, 333]. This results in two types of correlated barrier hopping mechanisms on application of an electric field. First type corresponds to long range inter-well hopping which involves the hopping of holes from Ni$^{3+}$ ion located in one defect potential well to Ni$^{2+}$ ion in an adjacent defect potential well. However, the second type is due to short range intra-well hopping of holes between ions located within one defect potential well. Moreover on applying the ac signal, the relative probability of occurrence of charge transfer mechanics depends on the (i) energy of the
charge carriers, (ii) frequency of the applied ac signal and (iii) concentration, depth, mean-site separation and percolation of the potential wells associated with Ni\(^{2+}\) ions \([255, 333]\). Generally NiO nanostructures possess high density of hopping charge carriers and thereby its dielectric constant at low frequency can be understood by defining the polarization \(P\) (dipole moment per unit volume) as:

\[
P = \sum_{\alpha} x_\alpha q_\alpha, \tag{7.6}
\]

where \(\alpha\) includes all the charged particles in the system, \(q\) represents the respective charges and \(x\) the displacement of the charges under an applied electric field. When the applied signal frequency is low, the charge transport mechanism is mainly through inter-well hopping of holes which corresponds to steady state transport of charge carriers between the electrodes and does not contribute to polarization. However, the high density of Ni\(^{2+}\) ions within the grain boundaries of NiO nanostructures extends the percolation of the adjacent defect potential wells \([334]\). This results in inter-well hopping of holes which reverse its direction on field reversal and cause dielectric relaxation at low frequencies. This reasoning is quite consistent with the results of conductivity studies of NiO nanostructures with high density of Ni\(^{2+}\) vacancies attributed to inter-well hopping of holes through mean-site separation of Ni\(^{2+}\) vacancies of orders of few nanometers \([324, 334]\). This result in very high polarization value and large dielectric constant of the order of \(10^2\) to \(10^4\) at low frequency attributed to inter-well hopping of charge carriers which reverses its direction of motion on field reversal. However as the signal frequency is increased to
very high value, the charge carriers cannot follow the field reversal and do not get enough time for long range hopping. As a result, the probability of intra-well hopping of charge carriers with average hopping distance of one lattice spacing ($\approx 4.2$ Å for NiO) becomes large. Since the hopping distance is quite smaller than the inter-well hopping distance, the polarization (according to Eq. 7.6) decreases with increase in signal frequency. When the signal frequency is further increased, the charge carriers barely start to move before the applied field reverses its direction. Consequently the dielectric constant falls rapidly to very small value lesser than single crystalline NiO due to accumulation of high density of holes at grain boundaries. Further the lattice contribution to dielectric constant is quite low ascribed to devoid of charge carriers at the grain interior which is supported by the reported studies on molecular dynamics and electrical nature of NiO grain boundaries [335–340]. Moreover, the dielectric loss shows very strong dependency on signal frequency than dielectric constant. When the applied signal frequency is low inter-well hopping mechanism is the predominant process and the dielectric loss is quite higher. This is because due to overlapping of defect potential wells only a small fraction of total holes undergoing long-range hopping reverses direction on field reversal and contribute to polarization. While the majority of holes contribute to dielectric loss due to steady transport of charges between the electrodes and consequently as the frequency decreases, there will be a sharp increase in dielectric loss than dielectric constant. In general two possible conduction mechanisms are present in NiO nanocrystals: grain boundary conduction due to proton hopping in adsorbed water layer and hole conduction in bulk [341]. FTIR analysis shows surface hydroxyl groups of nanocrystals which causes proton conductiv-
ity (Fig. 7.7). However for nanocrystals of critical size (< 9 nm) with defects, conductivity is mainly due to hopping of holes [341]. This is corroborated from the impedance spectra of NiO samples (Fig. 7.9). As per correlated barrier hopping model [326], the bulk conductivity of NiO nanocrystals is mainly attributed to hopping of charge carriers through nickel vacancies and is determined using the equation:

\[
\sigma = \frac{d}{R_b A} S \text{cm}^{-1},
\]

(7.7)

where \(d\), \(A\) and \(R_b\) are thickness, area and bulk resistance of sample pellets respectively. Studies confirm that higher defect density lowers the conductivity by trapping charge carriers at nickel vacancies [324, 342]. Fig. 7.9 shows that bulk resistance of sample B is approximately twice that of A. This is attributed to higher density of nickel vacancies (Ni\(^{2+}\)), which increases the hopping distance of charge carriers [343]. Higher resistance lowers the mobility of charge carriers and decreases the conductivity as confirmed by Figs. 7.9 and 7.10a. The relaxation frequency \(\omega_{\text{max}}\) (frequency corresponding to maximum of \(Z''\)) of sample A is blue shifted as compared to B (Fig. 7.10b). Higher relaxation frequency of A indicates lower relaxation time (\(\tau\)) of charge carriers and hence results in higher conductivity. In the present case the most probable relaxation time of charge carriers of A and B are \(~ 22 \mu s\) and \(~ 53 \mu s\) respectively. In addition surfactants also have an effect on dielectric property of nanocrystals. In PVP assisted synthesis, less defects of nanocrystals results in high dielectric constant as shown in Fig. 7.11a. However, the dielectric loss of A (Fig. 7.11b) is significantly higher than B due to its higher conductivity. This is ascribed
to lower probability of charge carriers trapping at defect centers. As a result, mobility and hopping of carriers are higher in sample A [324, 342]. In order to confirm this, hopping frequency of charge carriers is analyzed by plotting tan$\delta$ as a function of angular frequency (Fig. 7.12). Both the samples exhibited dielectric relaxation corresponding to maximum dielectric loss at specific frequency which is same as the hopping frequency of charge carriers. From Fig. 7.12, it is found that hopping frequency of sample A is $\sim 2.902 \times 10^3$ s$^{-1}$ and that of B is $1.08 \times 10^3$ s$^{-1}$. Since hopping frequency is directly proportional to its hopping probability, charge carriers in sample A have higher hopping probability than B [344]. This study shows that type of surfactant plays a major role in altering electric and dielectric properties of NiO nanocrystals.

### 7.5 Conclusion

The influence of PVP and CTAB on electrical and dielectric properties of nickel oxide nanocrystals synthesized by chemical precipitation method is studied. Photoluminescence spectroscopy analysis reveals that nanocrystals synthesized using PVP shows emission in visible region, whereas CTAB assisted nanocrystals exhibits UV emission. This variance is attributed to the fact that PVP induces lesser defects in nanocrystals due to slower nucleation rate which accelerates growth of nanocrystallites along preferred lattice direction. On the other hand lattice dislocations appear to be higher with nanocrystals synthesized using CTAB. Moreover the emission in UV region is due to high density of Ni$^{2+}$ ions. The electric and dielectric studies show that the properties are significantly influenced by microstrain of nanocrystals. The bulk resistance
and relaxation time of charge carriers is higher for nanocrystals having larger microstrain and defects. Conversely the dielectric relaxation frequency showed a blue shift for nanocrystals with less microstrain and point defects. This indicates higher hopping probability of charge carriers which leads to increased conductivity. Hence the electrical and dielectric properties of nanocrystals can be tuned for specific applications by merely varying the type of surfactant.