

Temperature Effects on the Magnetic Properties of NiO Nanoparticles

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Abstract - NiO nanoparticles were synthesized by hydrothermal method with different annealing temperatures (350-550°C). The structural, morphological, optical and magnetic properties of synthesized nanoparticles were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), UV-visible spectroscopy, photoluminescence (PL) and vibrating sample magnetometer (VSM). The XRD result confirms the high purity, spherical cubic phase NiO nanoparticles with high crystal quality. The energy gap of the NiO nanoparticles found to be decrease with increase in annealing temperature ($E_g=3.71-3.65\text{eV}$) and broad absorption in the range of 331 nm indicates the quantum confinement effect. PL peaks were observed at 417 and 437 nm and an enhancement in the PL intensity was observed with increase in temperature. The magnetic properties of these nanoparticles confirming the ferromagnetic behavior at room temperature and has been attributed due to particle size effect.

Index terms: NiO, Photoluminescence, Energy gap and VSM studies.

I. INTRODUCTION

Transition metal oxides are indicated as an interesting class of materials because of their potential applications as catalysts, sensors, and photochromic devices[1]. Among various transition metal oxide nanoparticles, NiO nanoparticles are most widely used in various industrial and medical applications because of its unique properties such as high stability, radiation, thermal resistance, low cost, wide availability, optical transparency and high piezoelectric properties etc[2]. Nickel oxide (NiO), a p-type semiconductor with wide band gap of 3.6 eV, is widely used in many fields such as gas sensors, electrochromic films, catalysis, fuel cell electrodes, and magnetic materials [3]. Because of its great physical and chemical properties, nanoscale NiO has attracted tremendous interest. The synthesis of NiO nanoparticles has been examined utilizing different synthesis routines, including molecular beam epitaxy (MBE), chemical vapor deposition (CVD), laser ablation, sol gel process, sputtering (SP) [4-8], vapor phase transport (VPT)[8], hydrothermal synthesis [9], Co-Precipitation Method[10], chemical bath deposition (CBD)[11] and solid state reaction method [12]. Among these methods hydrothermal method has been widely studied as because it is relatively simple and inexpensive.[9]

In the present work, NiO nanoparticles were synthesized by simple hydrothermal method by using nickel chloride as a precursor at different temperatures. The structural morphological, optical and magnetic properties of the synthesized NiO nanoparticles were investigated.

II. EXPERIMENTAL PROCEDURE

The NiO nanoparticles were synthesized by using nickel chloride hexahydrate as precursor. 2.37g of nickel chloride hexahydrate was taken to dissolve in 50ml of deionized water and then stirred by magnetic stirring apparatus at room temperature. 20ml of aqueous ammonia solution was gradually added dropwise in the solution. The resultant solution was continuously stirred for 24h. Finally the green color precipitate appears. The resulting precipitate was filtered, and washed several times in deionized water and ethanol. Green precipitates were dried at 100°C for 4 h in oven. The samples were annealed at 350°C for 1 h to get the black NiO nanoparticles. Similar procedure has been

repeated for different annealing temperatures such as 400°C, 450°C, 500°C and 550°C.

The crystal structure and phase of NiO nanoparticles were characterized by X-ray diffraction (SHIMADZU-XRD 6000) analysis. The morphology of the NiO nanoparticles was analyzed by Scanning electron microscopy (Hitachi S-4500 SEM machine). The absorption spectra were measured using UV-Vis spectrophotometer (SHIMADZU-UV 1800). PL study was carried out at room temperature using a VARIAN spectrophotometer equipped with a 450 W Xenon lamp as the excitation source. Fourier transform infrared (FT-IR) spectra were recorded in the range 4000–500 cm^{-1} using a BRUKER: RFS 27. FT-Raman spectra were recorded at room temperature using the same instrument using 100 nm excitation laser over a wave numbers range of 50–3700 cm^{-1} . The magnetic measurement was carried out in a vibrating sample magnetometer (lakeshore VSM 7140) at room temperature.

III. RESULTS AND DISCUSSION

A. STRUCTURAL ANALYSIS:

The XRD analysis was employed to determine the structure and phase of NiO nanoparticles prepared at different temperatures (350–550°C) shown in Figure 1. The diffraction peaks at $2\theta = 43.09, 37.04, 62.71, 75.27, 79.24$ are corresponding to the Miller indices (2 0 0), (111), (2 2 0), (311), (2 2 2) planes are observed. The peaks in the XRD patterns can be indexed to be a cubic pure phase of NiO [JCPDS card No:65-2901]. No other peaks are detected within the detection limit of the XRD instrument.

The intensity of the peaks increases with increase of temperatures. The intense and sharp peaks demonstrate that the as-obtained products are well-crystallized [13]

The average crystallite size has been inferred from 2θ and the full width at half maximum (FWHM) of the (h k l) peaks using Debye–Scherer relation.[14, 15] The XRD peaks are sharp and intense which ensure the well crystallized structure of the nanoparticles. The calculated average crystallite size, dislocation density, micro strain and stacking faults value of each peak are listed in Table 1&2. It is observed that the crystallite size gradually increases with increase in the annealing temperature (350–500°C) [16].

Table .1 Structural parameter of NiO nanoparticles formed at different temperature (111) plane

Temperature °C	Crystal size D nm	Dislocation density $\delta \times 10^{14}$	Micro strain ϵ
350	12.10	68.3013	0.00326
400	13.35	56.1096	0.00271
450	13.71	53.2016	0.00259
500	13.94	51.4606	0.00201
550	13.86	52.0563	0.00232

Table .2 Structural parameter of NiO nanoparticles formed at different temperature (111) plane

Temperature °C	Stacking Fault	Lattice Constant Å
350	0.005648	4.228
400	0.004696	4.208
450	0.005282	4.194
500	0.004494	4.182
550	0.004491	4.204

However, the enhancement of crystalline is correlated to the increase in crystal size.

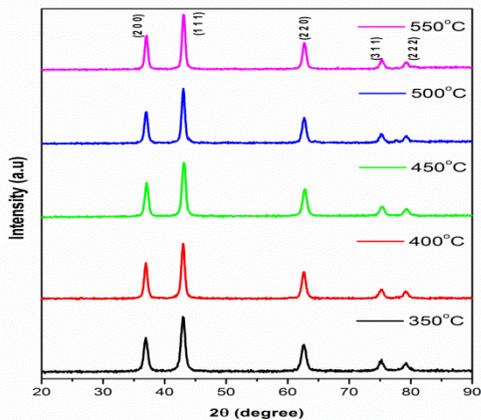


Fig .1 XRD pattern of NiO nanoparticles formed at different temperature 350- 500 °C

Increasing the temperature above 550°C results similar NiO cubic phase with reduction in the size of the

NiO nano particles, because the heat treatment to involve changes in crystallite size and stabilizes a more face centered cubic (FCC) structure according to the size effect. The grain size increases with increase in temperature(350 to 500°C) [17]. This behavior was expected because the heating facilitates the diffusion and agglomeration of the particles. The diffraction peaks becomes more intense and it can be attributed to the thermally promoted crystallite growth. Calcinated temperature clearly promotes grain growth with further increasing in annealing temperature (550⁰ C) [18]. When the particle size reduces, the surface-to-volume ratio and so the surface atoms in the nanoparticles increase. This can improve the surface reaction of the nanoparticle [19].

Grain growth results in size effects and induces the transformation of NiO during annealings in air. The calculated lattice constant values are less than the standard value which is the strong indication of stress in the nanoparticles. The lattice defects like δ , ϵ and SF showed a decreasing trend with increasing temperature from 350 to 500°C which may be due to the improvement of crystallinity as well as the high orientation along (111) direction [20].

B.FUNCTIONAL GROUP ANALYSIS

Figure.2 shows the FT-IR spectra of the NiO nanoparticles synthesized at different annealing temperature (350–550°C).

Various compositional elements and their bonding nature present in the synthesized NiO nanoparticle were analyzed by FTIR spectra.

The high intense broad band peaks at 400-600 cm⁻¹ are assigned to NiO molecule, which is due to the vibration mode of metal and oxygen molecules. The broad peak at 1599 cm⁻¹ is due to the H-O-H bending vibration. Peaks at 1380 cm⁻¹ corresponds to the C-O stretching vibration . 1000-1500 cm⁻¹ are due to the anti symmetric stretching and symmetric stretching mode of vibrations of CO₂ molecule absorbed from air. The broad peaks at 3432cm⁻¹ is to due to the stretching vibrations of OH-group.

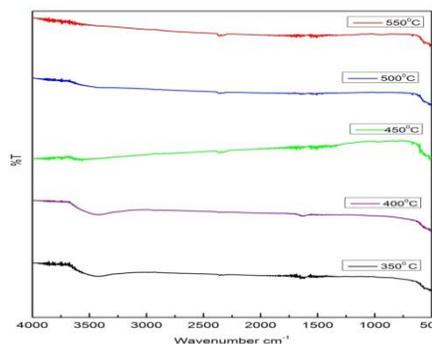


Fig 2. FTIR spectra of NiO nanoparticles synthesized at various temperatures 350–550°C

C. SURFACE MORPHOLOGY ANALYSIS

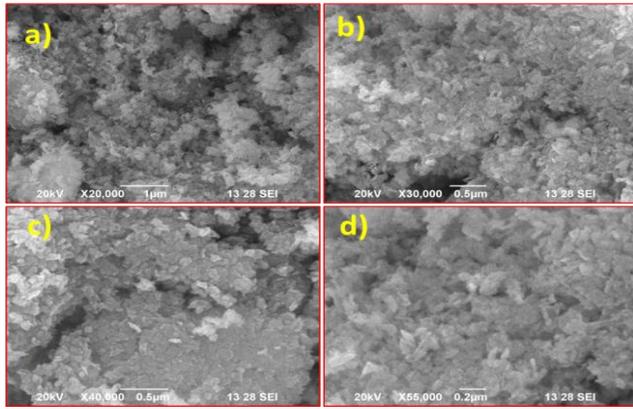


Fig.4. (a-d) SEM images of NiO nanoparticles annealed at 450°C with different magnifications

The SEM techniques were used to examine the shape and size of synthesized NiO nanoparticles. SEM image of NiO nano particles at different magnification is shown in **Figure 4 (a-d)**. From the figure, we can observe that the particles were agglomerated with irregular spherical shaped nanoparticles[18] and the particles size was in the range of 12-14 nm. Some of the particles are in spherical shape. The particles are uniformly distributed and attached to each other to form agglomerated particles.

The chemical composition of the NiO nanoparticles has been studied using energy dispersive X-ray (EDX) analysis and the EDX pattern is shown in **Figure 5**.

Table 3. Compositional analysis of NiO nanoparticles

Elements	Atomic number	Series	Weight %	Atomic %
Ni	28	L-series	68.74	37.47
O	8	k-series	31.26	62.53

The result shows the presence of 68.74% of Ni and 31.26 % of O (Table. 3). It was observed that the nanoparticles are composed of nickel and oxygen only.

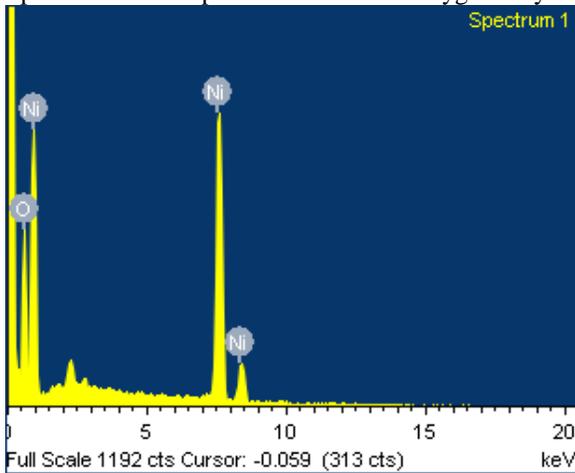


Fig.5 EDAX spectra of NiO nanoparticles annealed at 450°C

D. UV-VIS SPECTROSCOPIC ANALYSIS

The UV-visible absorption spectrum of NiO nanoparticles annealed at different temperature (350-550 °C) in the wavelength range of 200 to 1100 nm is shown in the **Figure 6**. The spectrum of NiO annealed at (450, 500 and 550 °C) shows a strong emission peak at 331 nm, it is well known that the UV emission peak (~329.5 nm) originates from the near band edge emission from the recombination of free excitons. The values are closely related with the values reported. The shifted weak blue emissions at (350 and 400 °C) might be due to surface defects in the NiO nanoparticles. All the samples have nearly (~331nm) absorption in the blue emission in ultra violet region. The optical band gap energy has been calculated using the following equation ,

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

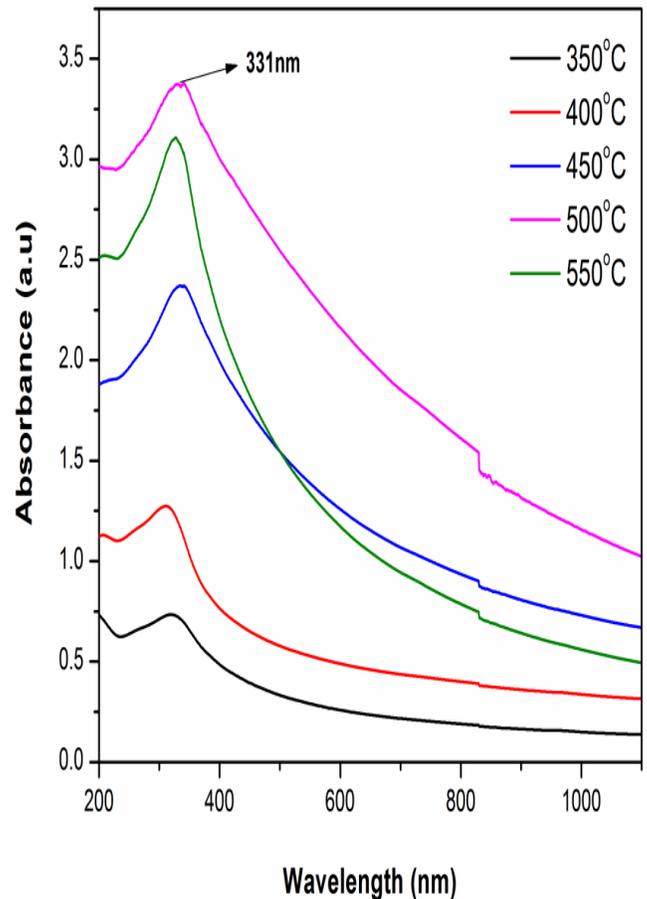


Fig.6 UV-vis absorption spectra of NiO nanoparticles at different temperatures (350-550 °C)

Figure7 shows the $(\alpha h\nu)^2$ vs. $h\nu$ plot of NiO nanoparticles. The band gap values have been determined by extrapolating the linear portion of the curve to meet the $h\nu$ axis. The optical band gap of the NiO nanoparticles has been calculated and is found to be 3.71, 3.69, 3.66, 3.63 and 3.65eV for 350°C, 400 °C, 450 °C, 500 °C and 550°C respectively. The band gap energy of NiO nanoparticles tends to fall as the temperature increases. This is because when temperature raises, the amplitude of atomic vibrations rises leading to more inter atomic spacing and leads to fall

in the optical band gap. This phenomenon has been described by the Brus' effective-mass model (EMM).

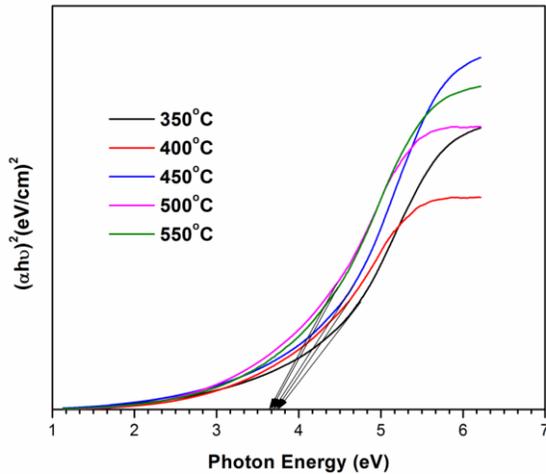


Fig.7 Band gap energy calculation graph of NiO nanoparticles at different temperatures (350-550 °C)

E. PHOTOLUMINESCENCE ANALYSIS

PL emission spectra for all the samples are measured in the wavelength range 360 to 650nm, and the spectrum is shown in **Figure8**. Two main emission peaks were revealed at about 417nm and 437nm wavelength in the blue emission band with different annealing temperature (350-500°C). The difference of the PL spectra is due to several annealing temperatures leading to the structure of different phases and surface microstructure. At 550°C, lowest PL intensity was due to the lower recombination of excited electrons and holes and the lower PL intensity demonstrates the reduction in the rate of recombination. The intensity of photoluminescence decreases with increasing temperature. This indicates a lower recombination rate of electron-hole pairs and hence higher separation efficiency. The heat treatment may result in a slight deviation from NiO interstitial oxygen trapping in the NiO nanoparticles are leads to two shoulders peaks at 417nm and 437nm in blue emission band, confirm The presence of such defects in NiO nanoparticles. A peak at 417 nm and 437 nm were observed in the absorption spectrum of NiO particles of present study and attributed to oxygen related defects. The values (~420 and 425nm) are closely related to the values reported.

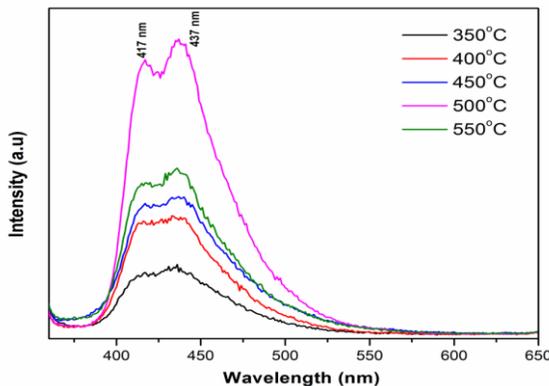


Fig.8

PL spectra of NiO nanoparticles prepared at different temperatures

F. MAGNETIC PROPERTIES

The magnetic properties of NiO nanoparticles with 450°C annealing temperature were measured by magnetic hysteresis loop using VSM at room temperature. Figure 9 shows the hysteresis curve of the NiO nanoparticle. The hysteresis loops of the present sample shows the ferromagnetic behavior with coercivity (465.88Oe), retentivity (11.96×10⁻³emu/g) and magnetization (0.21emu/g). The magnetic measurements shows that when the size of the particles is reduced to nanoscale, the antiferromagnetic NiO nanoparticles can exhibit the ferromagnetic properties. High coercivity was observed for the NiO nanoparticles with respect to the size of 13.71 nm which is agreed well with the earlier report. This is due to the ferromagnetic arrangement of uncompensated spins on the surface of the samples due to the reduced particle size.

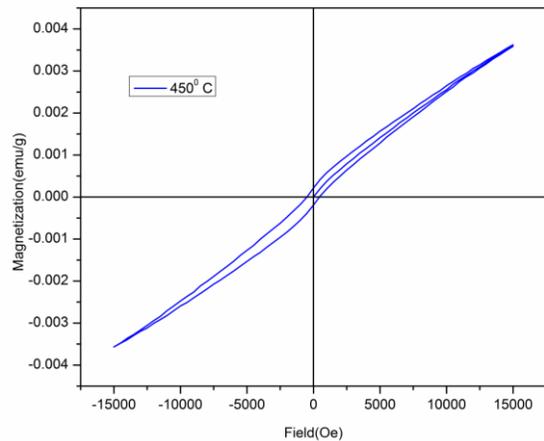


Fig.9 Hysteresis curves of undoped NiO nanoparticles

IV. CONCLUSIONS

In summary, nanocrystalline of NiO have been synthesized by introducing different annealing temperatures through simple hydrothermal methods. XRD analysis revealed the formation of single phase cubic NiO structure and their nanocrystalline nature. SEM analysis revealed the surface morphology of samples which attain smoothness due the fine geometry of Ni²⁺ ion. The elemental composition of Ni and O was confirmed by EDX report. PL emission spectra showed a relative increases with increase of annealings temperature. The optical band gap energy decrease with increase of annealings temperatures to found (3.71-3.65eV). From the structural and optical properties of the samples, It is concluded that NiO is useful in the magnetic applications and can be suggested as suitable candidate for the supercapacitors applications.

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