Comparative study of the structural and optical behaviours of Co and Ni doped ZnO nanocomposites

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Abstract - **The development of rapid and reliable processes for the synthesis of Nanomaterials is of great importance in the field of Nanotechnology. Generally, Nanotechnology deals with structures sized between 1 to 100 nm in at least one dimension, and involve developing materials or devices with a vast range of applications such as medicine, electronics, biomaterials and energy production. In material science, the Cobalt and Nickel doped Zinc Oxide nanocomposite is being used for various applications. The comparative study of Structural and Optical behaviours of Co and Ni doped ZnO nanocomposites have been studied in this work. The nanocomposites are prepared by annealing at 500oC. The synthesised composites are characterized by using XRD, TEM, SEM, EDAX, IR, UV-Vis and PL.**

keywords - **Nanocomposites, Optical behaviours, annealed, EDAX analysis**

I. INTRODUCTION

Nanotechnology is the study of manipulating matter of an atomic and molecular scale. Generally, nanotechnology deals with structures size between 1 to 100 nanometre in at least one dimension, and involve developing materials or devices within that size. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, bio materials and energy production, magnetic solar media, Semiconductors, solar energy transformation, electronics and catalysis [1-9].

Nanomaterials show properties distinct from bulk materials because of the nature of the atomic structure in the interfacial regions separating nanoparticles. The dielectric property of nanocrystalline materials exhibit unusual properties that play vital role in the development of new materials.

A nanocomposite organic/inorganic material is one among the fast growing areas of research. The oxides of transition metals belong to important class of semiconductors, which have applications in magnetic solar media, solar energy transformation, electronics and catalysis.

ZnO is an II and VI compound semiconductor. The crystal structures shared by ZnO are Wurtzite, Zinc blend and rock salt. At ambient conditions, the thermodynamically stable phase is Wurtzite. The Zinc blended ZnO structure can be stabilized only by growth on cubic substrates and the rock salt.

ZnO is not really a newly discovered material. Research on ZnO continued many decades with interest following a roller coaster pattern. The semiconductor has gained substantial interest in the research community in part because of its large excitonic binding energy (600 meV) which could lead to lasing action based on excitonic recombination above room temperature semiconductor field with studies of its lattice parameters.

Recently, II and VI semiconductor nanoparticles have been extensively studied for their applications in displays, high density storage devices, energy storage devices, Photovoltaic, biological labels etc [10-12]. One of the major efforts is on optimizing the emission properties of the wide band gap II – IV semiconductor materials due to the increasing demand for high brightness light sources operating in the Ultra Violet (UV) region.

Among the II – VI wide band gap semiconductor materials, ZnO is one of the most promising candidates for the UV emitter applications due to its wide band gap of 3.37eV at (300 K) and a high excitonic binding energy of 60 meV when compared to GaN (21-25meV); the possibility of wet chemical processing; and resistance to radiation damage.

ZnO has numerous attractive characteristics for electronics and optoelectronics devices [13-15]. The higher excitonic binding energy enhances the luminescence efficiency of light emission. The room temperature electron Hall mobility in single crystal ZnO is ~ 200 cm^2 V^{-1}, singly lower than that of GaN, but ZnO has higher saturation velocity. ZnO has exhibited better radiation resistance than GaN for possible devices used in space and nuclear applications.

II. SIGNIFICANCE OF THE WORK

Comparative Study of synthesizing metal oxide nanocomposites and their characterizations has attracted attention of scientific community for more than centuries. The different behaviours can be studied by structural and optical properties. Here in this present work interesting results have been found out about the structure of the compound and composites. As well the nanocrystalline nature of the synthesized particles was confirmed with the experimental calculations.

In materials science, the Cobalt, Nickel doped Zinc Oxide nanocomposites [16-24] are being used for various applications. The synthesis and characterization of Cobalt, Nickel doped Zinc Oxide nanocomposite and its structural and optical properties have been studied in this work.

Microwave technique has been used as the synthesis technique for the Solvothermal method for the synthesis of doped M-O nanocrystals. The synthesized samples are first tested for their crystallinity using XRD, TEM, SAED, SEM, EDAX, and functional groups and optical studies using FT -IR, UV – Vis, and PL. Band gap energies were calculated using UV – visible Spectrophotometer. Functional groups were identified using FT – IR Instrument. These are found to be much useful to gain a complete knowledge of the Structural and Optical properties of the systems. The study of Structural and Optical properties plays an important role in the transition Cobalt and Nickel doped metal Oxide nanocomposite.

III. CHEMICALS REQUIRED

All reagents used were of analytical purity and were used without further purification (CDH make). Zinc acetate dihydrate (Zn $(OAC)_2.2H_2O$)., Cobalt acetate tetra hydrate (Co $(ACO)_2.4H_2O$) and Nickel nitrate hexahydrate. Urea was used as a precursor. Ethylene glycol was employed as a solvent for all preparations. In a typical synthesis of Co doped ZnO nanocrystals, the required amount of Zinc acetate and urea were dissolved in the solvent in the stoichiometric ratio 1:3.

IV. SYNTHESIS OF COBALT AND NICKEL DOPED ZINC OXIDE NANOCOMPOSITES BY SOLVOTHERMAL METHOD

Analar grade Zinc acetate, Cobalt acetate, Nickel acetate hexahydrate and Urea along with Ethylene glycol were used for the preparation of Zn_XCo_{1-X} O and $ZnXNi_{1-X}$ O nanocrystals. Zinc acetate and cobalt acetate taken together in the required composition and 1:3 molecular ratios were mixed and dissolved in 50 ml Ethylene glycol and kept in a microwave oven by Solvothermal method. Microwave irradiation was carried out till the solvent was evaporated completely. The colloidal precipitate was obtained, cooled and washed several times with water and then with acetone to remove the organic impurities present, if any. The sample was then dried and collected. The following ratios were prepared: $Zn_{0.1}Co_{0.9}O$ and $Zn_{0.1}Ni_{0.9}O$. The samples were annealed at 500^0 C.

V. RESULTS AND DISCUSSION

5.1. Structural Property:

5.1.1 XRD Patterns of Cobalt and Nickel doped Zinc Oxide nanocomposites:

Fig 5.1 and 5.2 shows that the XRD Patterns of Cobalt and Nickel doped Zinc Oxide nanocomposites.

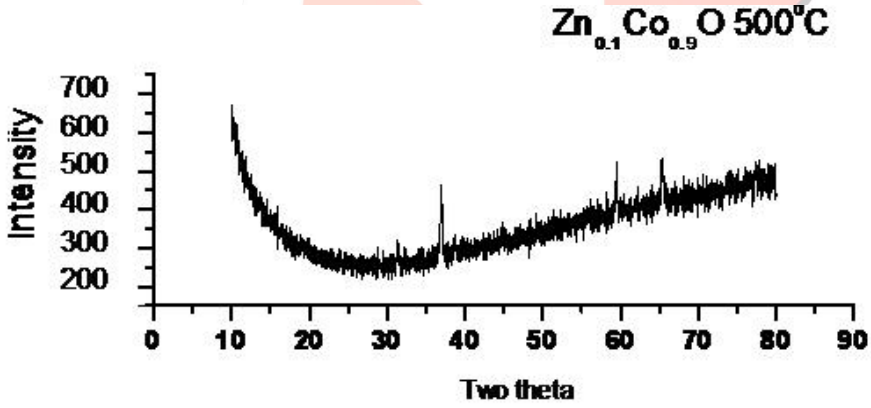

Figure 5.1: X – ray diffraction of $Zn_{0.1}Co_{0.9}O$ nanocomposites

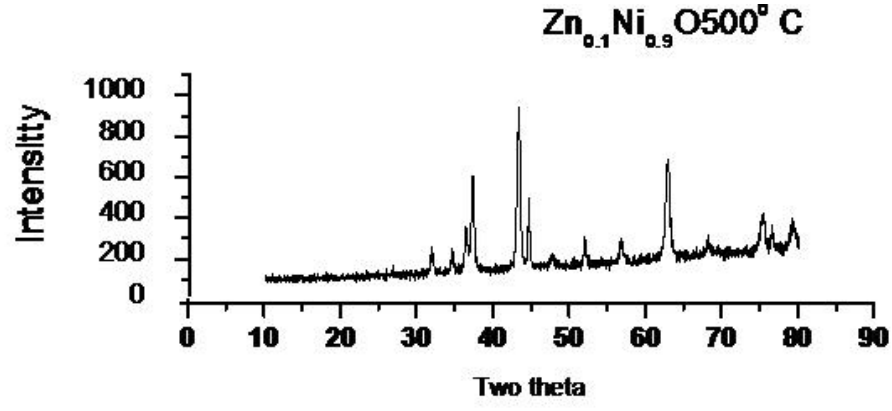

Figure5.2: X – ray diffraction of $Zn_{0.1}Ni_{0.9}O$ nanocomposites

Diffraction Studies reveal that the two samples are crystalline nature. It gives a secondary phase of CoO with hexagonal structure and NiO with cubic structure. The lattice parameters of CoO are a=b=3.21, c= 5.24 and NiO are a=b=c= 4.1887. The intensities and positions of the peaks are in good agreement with literature values (JCPDS file No.89-8399) and (JCPDS file No.89-3080). The broadening of the peaks indicates that the crystal size is small. Table 1 shows that the particle size of cobalt and Nickel doped Zinc Oxide nanocomposites. The size of $Zn_{0.1}Co_{0.9}O$ and $Zn_{0.1}Ni_{0.9}O$ nanoparticles are estimated to be calculated as 47 nm and 53 according to the Debye-Scherer formula.

Table 1. Particle size of Cobalt and Nickel doped ZnO nanocomposites

Sample	Particle Size (nm)
$Zn_{0.1}Co_{0.9}O$	47
$Zn_{0.1}Ni_{0.9}O$	53

Table 2shows the lattice parameter values for Co and Ni doped ZnO nanocomposites. Lattice parameter values are calculated using XRDA Software. It is good agreement with the standard values of JCPDS files.

Table 2. Lattice parameter values for Co and Ni doped ZnO nanocomposites

Sample	Crystal	Structure	Lattice parameter	Volume Cm^3
$Zn_{0.1}Co_{0.9}O$	CoO	Hexagonal	a = 3.21 b = 3.21 c = 5.24	42.96
$Zn_{0.1}Ni_{0.9}O$	NiO	Cubic	a = 4.1887 b = 4.1887 c = 4.1887	73.736

Sajid Husain et.al., [25] shows the intensity of Co and NiO peak increases with increasing cobalt nickel amount. The phase segregation has occurred and such structural degradation in the ZnO lattice may be attributed to introduction of a foreign impurity.

5.1.2 TEM and SAED

The structures of nanoparticles are investigated by TEM and SAED pattern. It is clearly seen from the TEM and SAED pattern. TEM and SAED were taken for the two samples. SAED patterns are also seen with good "hkl" plane values [26]. The cobalt doped ZnO TEM images and SAED Patterns are shown in Figure 5.3. On seeing the TEM images it is evident that the crystal sizes are almost in good agreement with the calculated size using the Debye Scherer's formula.

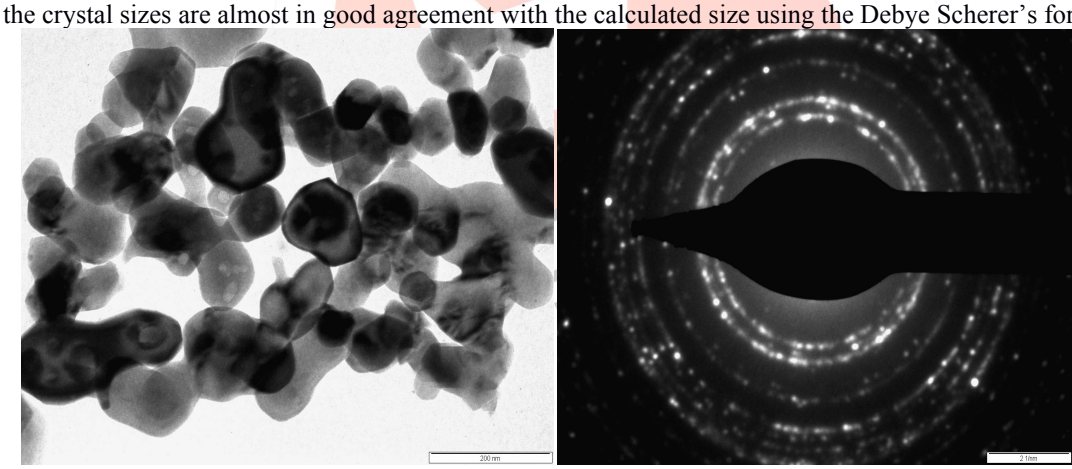

Figure5.3: TEM and SAED patterns of Cobalt doped ZnoNanocomposite

TEM images and SAED pattern of Nickel doped ZnO nanoparticles are as shown in Figure 5.4. The particle sizes are calculated approximately 50 nm.

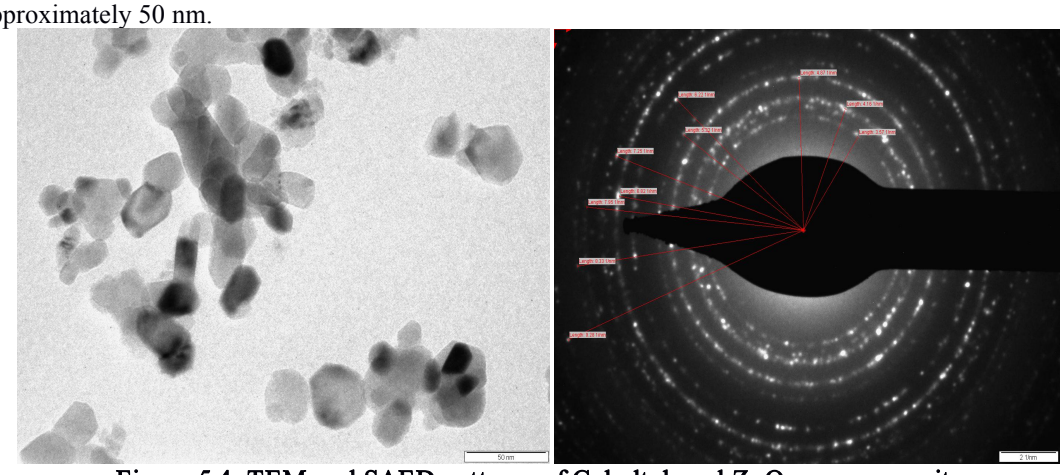

Figure 5.4: TEM and SAED patterns of Cobalt doped ZnO nanocomposite

5.1.3. SEM and EDAX

The surface morphology and elemental composition were investigated by SEM and EDAX. SEM images of Cobalt and Nickel doped ZnO samples, the thickness of the film is very thin so that one could get crystalline out of these samples. In some other images, segregated particles are seen with almost uniform spherical sizes. Because of the moisture is present in some of the samples. SEM images of cobalt and Nickel doped ZnO nanoparticles are shown in the Figure 5.5.

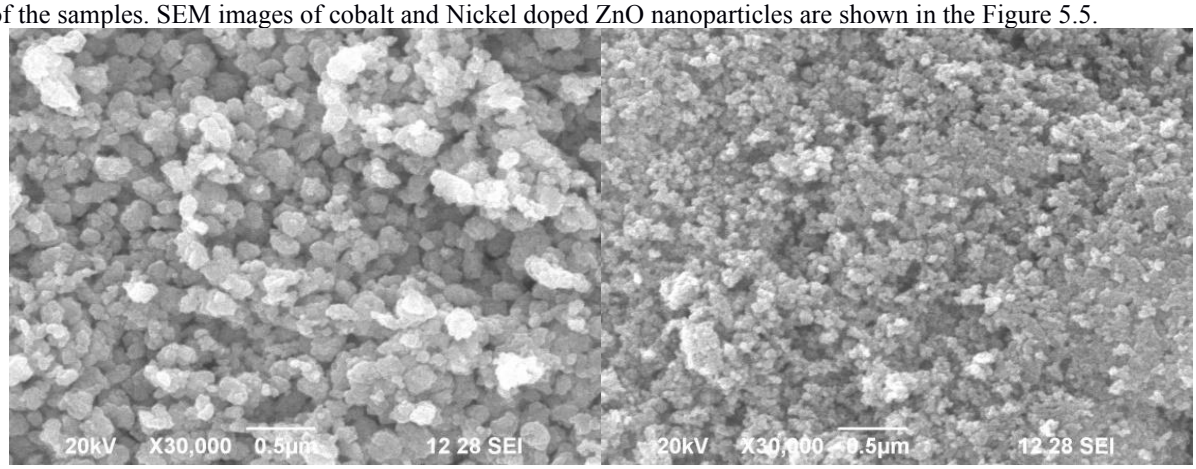

Figure 5.5: SEM images of Cobalt and Nickel doped ZnO nanoparticles

EDAX Analysis:

The energy dispersive X – ray analysis of the Copper and Nickel doped metal oxide nanocomposites are shown in the following Figure 5.6. It is evident from the x – ray patterns all the dopants are found in the respective spectrum. In addition to that interestingly it is observed there are no foreign materials present in the spectrum. It is an added confirmation for the purity of the samples. Tables 3 and 4 shows that the Quantitative analysis of Co and Nickel doped ZnO.

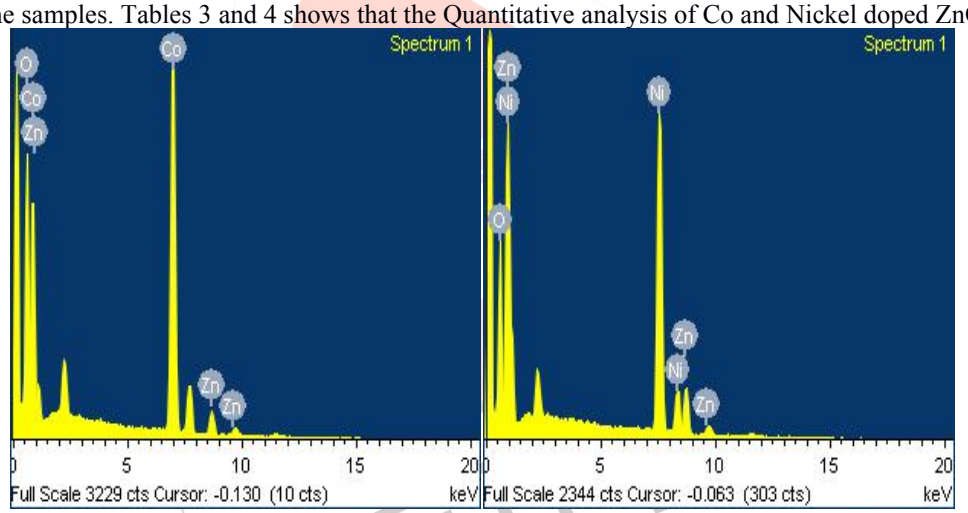

Figure 5.6: Energy dispersive X – ray analysis of the Copper and Nickel doped metal oxide nanocomposites.

Table 3. Quantitative analysis of Co-doped ZnO

Element	Wt %	At %
O k	30.25	41.70
Co K	61.90	34.31
Zn K	7.85	3.92

Table 4. Quantitative analysis of Ni -doped ZnO

Element	Wt %	At %
O k	21.81	51.11
Ni K	62.21	39.72
Zn K	15.98	9.16

5.2 Optical Properties

5.2.1 FTIR analysis:

The middle FT-IR spectrum of Co and Ni doped ZnO is shown in Figures 5.7 and 5.8.

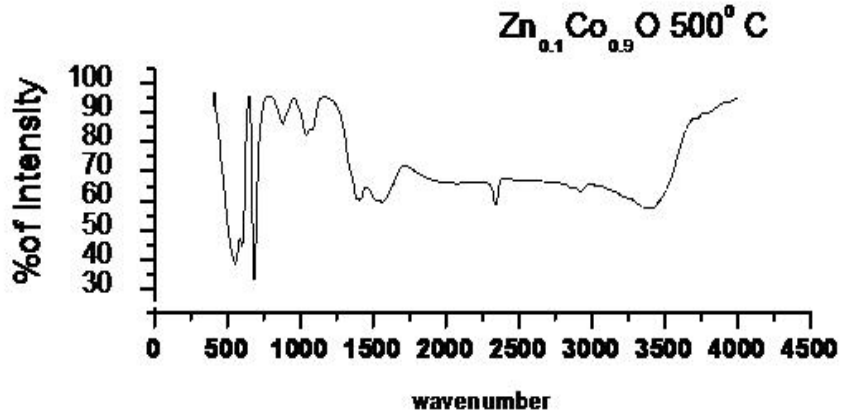

Figure 5.7: FT-IR spectrum of Co doped ZnO

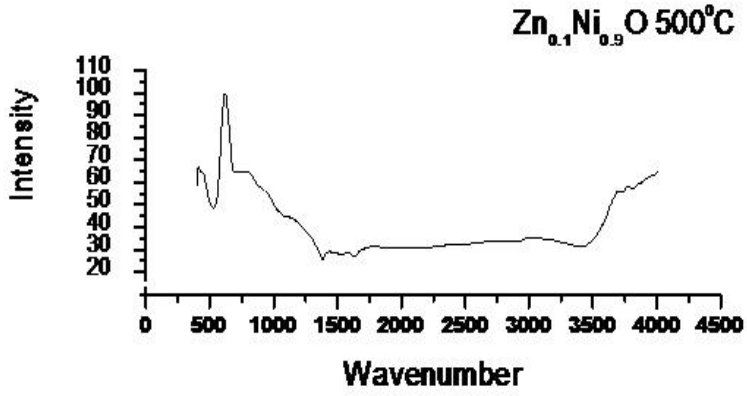

Figure 5.8: FT-IR spectrum of Ni doped ZnO

The peak at 3402 cm^{-1} and 3434 cm^{-1} corresponds to OH group of trace water which was adsorbed on the surface of ZnO [257, 258]. The presence of water is once again confirmed by its bending mode at 1626 $cm^{-1}$and 1631 cm^{-1}. The presence adsorbed ethylene Glycol CH_2 is also confirmed by its bending mode at 1381 cm^{-1}. The sharp peak around at 500 cm^{-1} might be due to Zn-O compound. Functional groups and their wave numbers are shown in the Table 5.

Table 5. Functional groups and their wave numbers

Functional groups	Wave numbers cm^{-1}
OH (Over tones)	3000 – 3600
OH (tones)	1631
CH_2	1381
M-O	500

5.2.2 UV – Vis absorption spectrum

Fig: 5.9 and 5.10 shows the UV – Vis absorption spectrum of Co and Ni doped ZnO nanoparticles.

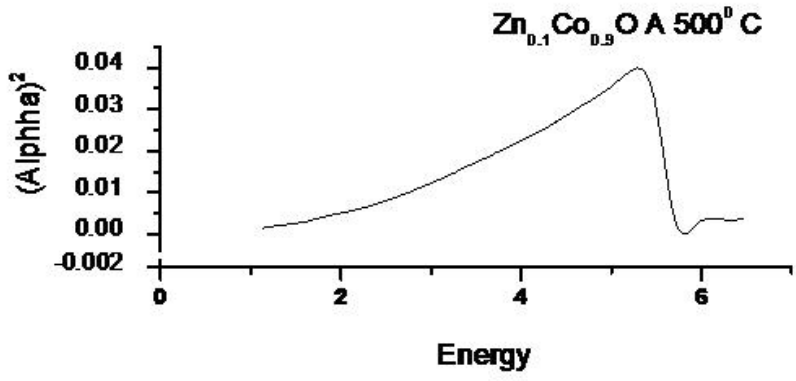

Figure 5.9: UV – Vis absorption spectrum of Co doped ZnO nanoparticles

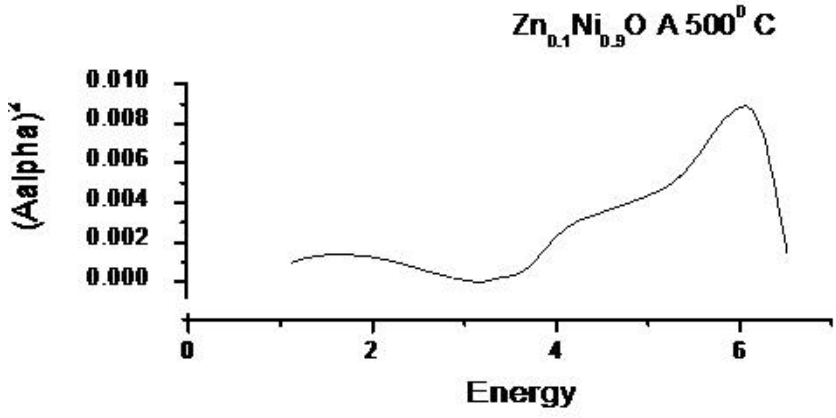

Figure 5.10: UV – Vis absorption spectrum of Ni doped ZnO nanoparticles

From the figure shows that the band gap energy calculation for Co and Ni doped ZnO nanocrystals. Table 6 shows that the band gap energy for Co and Ni doped ZnO nanoparticles. The band gap energy of the bulk ZnO nanomaterials was 3.2 eV at room temperature in our work the band gap energy at 3.0 and 3.17 eV for Co and Ni doped Zno nanoparticles. The bandgap energy is found to be increasing with dopant ratio. It is in good agreement with the previous work. [27].

Table 6. Band gap energy for Co and Ni doped ZnO nanoparticles

Sample	Band gap energy (eV)
$Zn_{0.1}Co_{0.9}O$	3.0
$Zn_{0.1}Ni_{0.9}O$	3.17

5.2.3 Photoluminescence Studies

PL specluim Co and Ni dopped ZnO nanoparticles are shown in Figures 5.11 and 5.12.

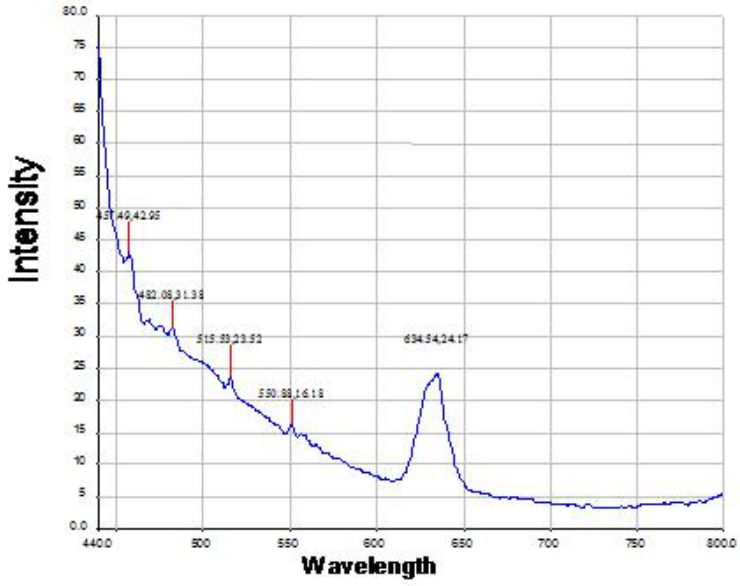

Figure 5.11: PL spectrum Co dopped ZnO nanoparticles

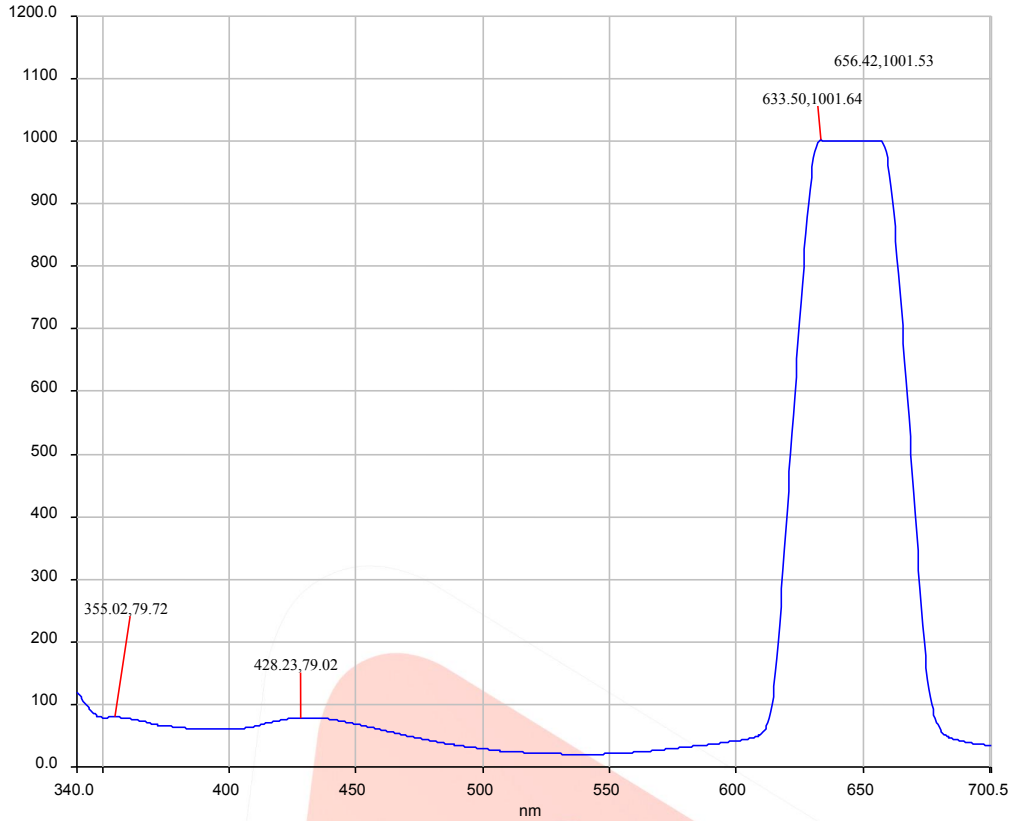

Figure 5.12: PL spectrum Ni dopped ZnO nanoparticles

Multiple peaks are observed in the PL region for Co and Ni doped ZnO nanocomposite. The band at 457 nm which may be owing to defect related emission. Another defect related emission in the blue region is observed at 473.44 nm. The relative PL intensity of UV emission is significantly enhanced in the Co^{2+} doped ZnO. Due to similar ionic radius of Zn as well as Co, the doping ion (Co^{2+}) is fully incorporated into the ZnO lattice. This broad UV emission is probably a reduction of the crystal quality by defects. A broad defect band is centred approximately 550 nm. The peak 633 indicates that the ZnO: Ni nanoparticles have good emission property and few defects.

V. CONCLUSION

Co and Ni doped nanocomposites with secondary phase of hexagonal and Cubic structure of CoO and NiO were synthesized successfully by Solvothermal method using microwave irradiation. From XRD, the particle size of nanoparticles was found to be 47 nm and 53 nm. The lattice parameter values are in good agreement with the standard values of JCPDS. Further the particle size was confirmed by TEM. It was evident that the crystal sizes are almost in good agreement with the calculated size using the Debye Scherer's formula. From SEM and EDAX the nanoparticles were seen with almost uniform spherical size. It was observed there are no foreign materials present in the spectrum. The functional group was determined by FT IR spectrum. In the higher energy region, there is a broad peak between 3000 – 3600cm^{-1}. It might be due to stretching of water. The broadening is a hydrogen bond between water molecules resting on ZnO surface. A broad band has been observed at around 500 $cm^{-1}$for the pure ZnO corresponding to the formation of ZnO bond. From UV- Vis, the band gap energy was increased with higher dopant ratio. From PL, the band at 457 nm which may be owing to defect related emission. Another defect related emission in the blue region is observed at 473.44 nm. The relative PL intensity of UV emission is significantly enhanced in the Co^{2+} doped ZnO. Due to similar ionic radius of Zn as well as Co, the doping ion (Co^{2+}) is fully incorporated into the ZnO lattice. The peak 633 indicates that the ZnO: Ni nanoparticles have good emission property and few defects.

VI. ACKNOWLEDGMENT

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